

FORM PTO-1390 (Modified)  
(REV 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

220583US0XPCT

U.S. APPLICATION NO (IF KNOWN, SEE 37 CFR

10/088505

INTERNATIONAL APPLICATION NO.  
PCT/JP00/06943INTERNATIONAL FILING DATE  
5 October 2000PRIORITY DATE CLAIMED  
5 October 1999 (earliest)

## TITLE OF INVENTION

PROPYLENE POLYMER, AND RESIN COMPOSITION AND MOLDED PRODUCT THEREOF

APPLICANT(S) FOR DO/EO/US

OKAMOTO Takuji et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☒ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☒ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

## Items 13 to 20 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Notice of Priority/PCT/IB/308/Form PTO-1449

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.101) <div style="font-size: 24pt; font-weight: bold; text-align: center;">10/088505</div>		INTERNATIONAL APPLICATION NO. <div style="font-weight: bold; text-align: center;">PCT/JP00/06943</div>		ATTORNEY'S DOCKET NUMBER <div style="font-weight: bold; text-align: center;">220583US0XPCT</div>	
24. The following fees are submitted: <b>BASIC NATIONAL FEE ( 37 CFR 1.492 (a) (1) - (5) ) :</b> <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... <b>\$1040.00</b> <input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... <b>\$890.00</b> <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... <b>\$740.00</b> <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... <b>\$710.00</b> <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... <b>\$100.00</b> <div style="text-align: right;"><b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b></div>				<b>CALCULATIONS    PTO USE ONLY</b>  <div style="border: 1px solid black; height: 100px; width: 100%;"></div>	
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				<div style="border: 1px solid black; padding: 2px;"><b>\$890.00</b></div> <div style="border: 1px solid black; padding: 2px;"><b>\$0.00</b></div>	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	30 - 20 =	10	x \$18.00	<b>\$180.00</b>	
Independent claims	6 - 3 =	3	x \$84.00	<b>\$252.00</b>	
Multiple Dependent Claims (check if applicable). <input type="checkbox"/>				<b>\$0.00</b>	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				<b>\$1,322.00</b>	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.				<b>\$0.00</b>	
<b>SUBTOTAL =</b>				<b>\$1,322.00</b>	
Processing fee of <b>\$130.00</b> for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				<div style="border: 1px solid black; padding: 2px;"><b>\$0.00</b></div>	
<b>TOTAL NATIONAL FEE =</b>				<b>\$1,322.00</b>	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). <input type="checkbox"/>				<div style="border: 1px solid black; padding: 2px;"><b>\$0.00</b></div>	
<b>TOTAL FEES ENCLOSED =</b>				<b>\$1,322.00</b>	
				<b>Amount to be refunded</b>	\$
				<b>charged</b>	\$
a. <input checked="" type="checkbox"/> A check in the amount of <u>          <b>\$1,322.00</b>          </u> to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>          <b>15-0030</b>          </u> . A duplicate copy of this sheet is enclosed. d. <input type="checkbox"/> Fees are to be charged to a credit card. <b>WARNING:</b> Information on this form may become public. <b>Credit card information should not be included on this form.</b> Provide credit card information and authorization on PTO-2038.					
<b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</b>					
<b>SEND ALL CORRESPONDENCE TO:</b>					
<div style="border: 1px solid black; padding: 10px; text-align: center;"> <b>Surinder Sachar</b>  <b>Registration No. 34,423</b>    <div style="font-size: 24pt; font-weight: bold;">22850</div> </div>			<div style="border-bottom: 1px solid black; margin-bottom: 5px;"> </div> <div style="margin-bottom: 5px;">SIGNATURE</div> <div style="border-bottom: 1px solid black; margin-bottom: 5px;">Norman F. Oblon</div> <div style="margin-bottom: 5px;">NAME</div> <div style="border-bottom: 1px solid black; margin-bottom: 5px;">24,618</div> <div style="margin-bottom: 5px;">REGISTRATION NUMBER</div> <div style="border-bottom: 1px solid black; margin-bottom: 5px;">March 28 2002</div> <div>DATE</div>		

## DESCRIPTION

### PROPYLENE POLYMER, AND RESIN COMPOSITION AND MOLDED PRODUCT THEREOF

#### Technical Field

The present invention relates to a propylene polymer, and a resin composition, a molded product and a resin modifier composed of the polymer. More particularly, the present invention relates to a propylene polymer capable of forming molded products having a less stickiness as well as excellent softness and transparency, a resin composition composed of said polymer, a molded product and a resin modifier.

#### Background Art

Although vinyl chloride resin has been widely used in the prior art as a soft resin, since vinyl chloride resins are known to generate harmful substances during the course of their combustion, there is a strong desire for an alternative product. Propylene polymer is an alternative to soft vinyl chloride resin. Propylene polymer has been produced in the presence of various catalysts. When propylene polymer produced using catalytic systems of the prior art are attempted to be made softer (namely to have a low elastic modulus), there is the shortcoming of an increase in the amount of sticky components. That is, conventional attempts for attaining soft polymers leads to the increase in APP components causing stickiness, resulting in poor surface characteristics of the resulting molded product. In addition, in the case where such a propylene polymer is formed into molded products such as sheets or films used in food, health care and other applications, there is the risk of causing various problems. Therefore, there is a need for a propylene polymer that offers an improved balance between elastic modulus and the amount of sticky components.

#### Disclosure of the Invention

The object of the present invention is to provide a propylene polymer capable of forming molded products having a less stickiness as well as



(mr) is a triad fraction.

5. A propylene copolymer satisfying the following (1) and (2):

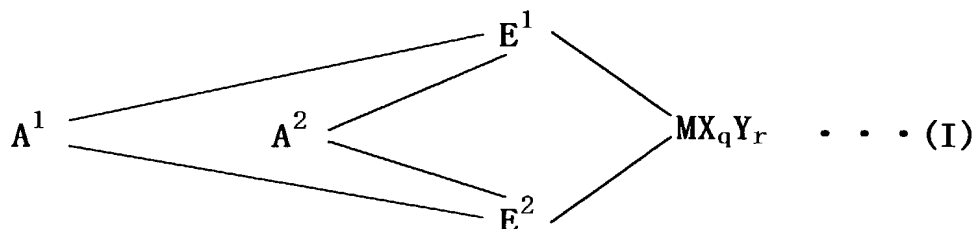
- (1) a stereoregularity index (P) of 55-90 mol% as determined by  $^{13}\text{C}$ -NMR measurement; and
- (2) a fraction (W25) eluted at a temperatures up to 25°C by temperature-programmed chromatography, of from 20-100 wt%.

6. The propylene homopolymer described in the above item 3 or 4, or the propylene copolymer described in the above item 5, having a molecular weight distribution (Mw/Mn) of 4 or less as measured by gel permeation chromatography (GPC) and/or an intrinsic viscosity  $[\eta]$  of 0.5-15.0 dl/g as measured at 135°C in tetralin.

7. The propylene homopolymer described in any one of the above items 3, 4 and 6, produced by polymerizing propylene in the presence of a polymerization catalyst comprising:

(A) a transition metal compound represented by the general formula

(I):



wherein M is a metal element of Groups 3 to 10 of the Period Table or lanthanoid series;

$\text{E}^1$  and  $\text{E}^2$  are respectively a ligand selected from the group consisting of substituted cyclopentadienyl, indenyl, substituted indenyl, heterocyclopentadienyl, substituted heterocyclopentadienyl, amide, phosphide, a hydrocarbon group and a silicon-containing group, which form a cross-linked structure via  $\text{A}^1$  and  $\text{A}^2$  and may be the same or different;

X is a ligand capable of forming a  $\sigma$ -bond or  $\pi$ -bond with the proviso that when a plurality of X groups are present, these groups may be the same or different, and may be cross-linked with the other X group,  $\text{E}^1$ ,  $\text{E}^2$  or Y;

Y is a Lewis base with the proviso that when a plurality of Y groups are present, these groups may be same or different, and may be cross-linked

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32

q is an integer of 1 to 5 given by the formula:  
 $[(\text{valence of M}) - 2]$ ; and  
 r is an integer of 0 to 3, and

8. The propylene copolymer described in the above item 5 or 6, produced by copolymerizing propylene with ethylene and/or a C<sub>4</sub>-C<sub>20</sub> α-olefin in the presence of a polymerization catalyst comprising:

$$\begin{array}{c}
 & & & E^1 \\
 & & & / \\
 A^1 & & & \\
 & & & \backslash \\
 & & & E^2 \\
 & & A^2 & / \\
 & & & \backslash \\
 & & & E^2 \\
 & & & / \\
 & & & MX_q Y_r \quad \cdot \cdot \cdot (I)
 \end{array}$$

E<sup>1</sup> and E<sup>2</sup> are respectively a ligand selected from the group consisting of substituted cyclopentadienyl, indenyl, substituted indenyl, heterocyclopentadienyl, substituted heterocyclopentadienyl, amide, phosphide, a hydrocarbon group and a silicon-containing group, which form a cross-linked structure via A<sup>1</sup> and A<sup>2</sup> and may be the same or different;

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that when a plurality of X groups are present, these groups may be the same or different, and may be cross-linked with the other X group, E<sup>1</sup>, E<sup>2</sup> or Y;

Y is a Lewis base with the proviso that when a plurality of Y groups are present, these groups may be same or different, and may be cross-linked with the other Y group, E<sup>1</sup>, E<sup>2</sup> or X;

A<sup>1</sup> and A<sup>2</sup> are divalent cross-linking groups capable of bonding the two ligands E<sup>1</sup> and E<sup>2</sup> to each other, are independently a C<sub>1</sub>-C<sub>20</sub> hydrocarbon group, a C<sub>1</sub>-C<sub>20</sub> halogen-containing hydrocarbon group, a silicon-containing group, a germanium-containing group, a tin-containing group, -O-, -CO-, -S-, -SO<sub>2</sub>-, -Se-, -NR<sup>1</sup>-, -PR<sup>1</sup>-, -P(O)R<sup>1</sup>-, -BR<sup>1</sup>- or -AlR<sup>1</sup>- wherein R<sup>1</sup> is a hydrogen atom, a halogen atom, a C<sub>1</sub>-C<sub>20</sub> hydrocarbon group or a C<sub>1</sub>-C<sub>20</sub> halogen-containing hydrocarbon group, and may be the same or different;

q is an integer of 1 to 5 given by the formula:

[(valence of M) - 2]; and

r is an integer of 0 to 3, and

(B) a component selected from the group consisting of (B-1) a compound capable of forming an ionic complex by reacting with the transition metal compound (A) or a derivative thereof, (B-2) aluminoxane, and (B-3) a Lewis acid.

9. A propylene resin composition comprising the propylene polymer, the propylene homopolymer or the propylene copolymer described in any one of the above items 1 to 8, and a nucleating agent.

10. A molded product produced by molding the propylene polymer, the propylene homopolymer, the propylene copolymer or the propylene resin composition described in any one of the above items 1 to 9.

11. A propylene resin modifier comprising the propylene polymer, the propylene homopolymer or the propylene copolymer described in any one of the above items 1 to 8.

12. A polymerization catalyst comprising:

(A) a transition metal compound represented by the general formula (II):

(B) a component selected from the group consisting of (B-1) a compound capable of forming an ionic complex by reacting with the transition metal compound (A) or a derivative thereof, (B-2) aluminoxane, and (B-3) a Lewis acid.

(A") a transition metal compound represented by the general formula (III):



wherein, M, X, Y, A<sup>1</sup>, A<sup>2</sup>, q and r are the same as defined in the above general formula (I); at least one of R<sup>8</sup> and R<sup>9</sup> represents a group containing a heteroatom such as oxygen, halogen and silicon; and R<sup>10</sup> through R<sup>17</sup> are respectively a hydrogen atom, a C<sub>1</sub>-C<sub>20</sub> hydrocarbon group, or a group containing a heteroatom such as oxygen, halogen and silicon, and

(B) a component selected from the group consisting of (B-1) a compound capable of forming an ionic complex by reacting with the transition metal compound (A) or a derivative thereof, (B-2) aluminoxane, and (B-3) a Lewis acid.

The propylene polymer [1], production method therefor [2], propylene resin composition [3], molded product [4] and propylene resin modifier [5] according to the present invention, are described in detail below.

The propylene polymer of the present invention is a polymer satisfying the following requirements (1) and (2):

$$\Delta H \geq 3 \times (T_m - 120).$$

The 25°C hexane soluble content (H25) of the propylene polymer of the present invention is 0-80 wt%, preferably 0-50 wt%, and more preferably 0-25 wt%. The H25 is an index showing a content of so-called sticky components causing defects such as stickiness and deteriorated transparency. The higher H25 means a larger content of the sticky components. When the H25 exceeds 80 wt%, the obtained polymer tends to be deteriorated in anti-blocking properties and transparency because of the large content of sticky components, and prevents the polymer from being used in food and health care applications.

[illegible]

wherein  $W_0$  is an initially measured weight of the propylene polymer; and  $W_1$  is a weight thereof measured after the propylene polymer is allowed to stand at 25°C for 3 or more days in 200 ml of hexane and then dried.

$$\Delta H \geq 3 \times (T_m - 120)$$

preferably,  $\Delta H \geq 2 \times (T_m - 100)$

The propylene polymer satisfying the above requirements enables production of a molded product that is well-balanced between an amount of sticky components, elastic modulus and transparency. That is, the molded product advantageously has a low elastic modulus, an amount of softness (also referred to as flexibility), less stickiness, excellent properties (typified by less bleeding of sticky components, less adhesion of sticky components to other articles and the like) and excellent transparency.

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10-way valve: Electric valve available from Balco Co., Ltd.; and  
Loop: 500  $\mu$ l loop available from Balco Co., Ltd.

fraction in pentad units in polypropylene molecular chain as measured using methyl signals in  $^{13}\text{C}$ -NMR spectra according to the method proposed by A. Zambelli et al., "Macromolecules", No. 6, p. 925 (1973). The larger value of the meso pentad fraction means a higher stereoregularity. When the meso pentad fraction (mmmm) of the propylene homopolymer of the present invention is less than 30 mol%, the polymer tends to become sticky. When the meso pentad fraction (mmmm) exceeds 60 mol%, the polymer tends to show a high elastic modulus. Also, the racemic pentad fraction (rrrr) means a racemic fraction in pentad units in polypropylene molecular chain. The value of  $[\text{rrrr}/(1 - \text{mmmm})]$  is determined from the above fractions in pentad units, and is an index indicating uniformity of the regularity distribution of the propylene homopolymer. The larger value of  $[\text{rrrr}/(1 - (\text{mmmm}))]$  means a broader regularity distribution, i.e., the polymer is present in the form of a mixture of a high-stereoregular polypropylene (PP) and amorphous polypropylene (APP) like conventional polypropylene produced in the presence of existing catalyst systems, so that the obtained polymer exhibits increased stickiness and deteriorated transparency. When the value of  $[\text{rrrr}/(1 - \text{mmmm})]$  of the propylene homopolymer of the present invention exceeds 0.1, the polymer tends to become sticky. The  $^{13}\text{C}$ -NMR spectra were measured according to the method for determining the attribution of peaks as proposed by A. Zambelli in "Macromolecules", 8, p.687 (1975), using the following apparatus and conditions:

Apparatus:  $^{13}\text{C}$ -NMR spectrometer "JNM-EX400 Model" available from Nippon Denshi Co., Ltd.;

Method: Proton complete decoupling method;

Sample concentration: 220 mg/ml;

Solvent: mixed solvent of 1,2,4-trichlorobenzene and heavy benzene (volume ratio: 90:10);

Measuring temperature: 130°C;

Pulse width: 45°;

Pulse repetition period: 4 seconds; and

Cumulative frequency: 10,000 times.

Next, the definition and the measuring method for W25 of the

propylene homopolymer of the present invention are the same as described in the above propylene polymer [1]. When the W25 is less than 20%, the propylene homopolymer fails to show a good flexibility.

Among the above requirements, the propylene homopolymer of the present invention preferably satisfies:

- (5) a meso pentad fraction (mmmm) of from 30 to 50 mol%;
- (6) a racemic pentad fraction (rrrr) satisfying the following formula:  
$$[\text{rrrr}/(1 - \text{mmmm})] \leq 0.08; \text{ and}$$
- (7) a fraction (W25) eluted at a temperatures up to 25°C by temperature-programmed chromatography, of from 30-100 wt%, more preferably satisfies:
- (8) a racemic pentad fraction (rrrr) satisfying the following formula:  
$$[\text{rrrr}/(1 - \text{mmmm})] \leq 0.06; \text{ and}$$
- (9) a fraction (W25) eluted at a temperatures up to 25°C by temperature-programmed chromatography, of from 50-100 wt%, and most preferably satisfies:
- (10) a racemic pentad fraction (rrrr) satisfying the following formula:  
$$[\text{rrrr}/(1 - \text{mmmm})] \leq 0.05; \text{ and}$$
- (11) a fraction (W25) eluted at a temperatures up to 25°C by temperature-programmed chromatography, of from 60-100 wt%.

In addition, the propylene homopolymer of the present invention is required to have (4) a pentad fraction (rmm) of more than 2.5 mol%. When the pentad fraction (rmm) exceeds 2.5 mol%, the obtained polymer is further increased in randomness and transparency. The propylene homopolymer of the present invention more preferably satisfies the following relationship:

$$(mm) \times (rr)/(mr)^2 \leq 2.0$$

wherein (mm) is a meso triad fraction; (rr) is a racemic triad fraction; and (mr) is a triad fraction.

This relationship expresses the degree of randomness of the polymer. The closer this value is to 1, the higher degree of randomness and transparency, and the better the balance between flexibility and elastic recovery ratio. For the propylene homopolymer of the present invention,

the value of the left side of the above equation is usually 2 or less, preferably 1.8-0.5, and more preferably 1.5-0.5. Furthermore, the triad fraction may be determined in the same manner as the above pentad fraction.

In addition to the above requirements, the propylene homopolymer of the present invention preferably has a molecular weight distribution (Mw/Mn) of 4.0 or less as measured by gel permeation chromatography (GPC), and/or an intrinsic viscosity  $[\eta]$  of 0.5 to 15 dl/g as measured at 135°C in tetralin. More preferably, the Mw/Mn is 3.5 or less and/or the  $[\eta]$  is 1.0-5.0 dl/g, and still more preferably, the Mw/Mn is 3 or less and/or the  $[\eta]$  is 1.0-3.0 dl/g. In particular, the  $[\eta]$  is still more preferably 1.2-3.0 dl/g, and most preferably 1.5-2.5 dl/g. When the molecular weight distribution (Mw/Mn) exceeds 4.0, the resulting polymer tends to become sticky. When the intrinsic viscosity  $[\eta]$  is less than 0.5 dl/g, the resulting polymer also tends to become sticky. When the intrinsic viscosity  $[\eta]$  exceeds 15.0 dl/g, the resulting polymer has poor moldability due to deteriorated fluidity.

Meanwhile, the value of Mw/Mn was calculated from values of weight-average molecular weight Mw and number-average molecular weight Mn which were measured in terms of polystyrene by gel permeation chromatography (GPC) using the following apparatus and conditions:

GPC: Column: TOSO GMHHR-H(S)HT;

Detector: RI Detector "WATERS 150C" for liquid chromatogram; and

Measuring conditions:

Solvent: 1,2,4-trichlorobenzene;

Measuring temperature: 145°C;

Flow rate: 1.0 ml/min.;

Sample concentration: 2.2 mg/ml;

Sample amount: 160  $\mu$ l;

Calibration curve: Universal Calibration; and

Analytic program: HT-GPC (Ver. 10).

In addition to the above requirements, the melting endotherm  $\Delta H$  of the propylene homopolymer is preferably 20 J/g or less as measured by DSC for excellent flexibility. The  $\Delta H$  is an index showing whether the polymer

is soft or not. The larger  $\Delta H$  means a higher elastic modulus and deterioration in flexibility. Meanwhile, the  $\Delta H$  is determined by the same method as described above.

Further, the propylene homopolymer of the present invention may or may not have a melting temperature ( $T_m$ ) and a crystallization temperature ( $T_c$ ). From the standpoint of flexibility, it is preferable that the propylene homopolymer has either no  $T_m$  and  $T_c$  or low  $T_m$  and  $T_c$ . More specifically, the  $T_m$  is, if measurable, preferably 100°C or lower. Meanwhile, the  $T_m$  and  $T_c$  are determined by DSC measurement using a differential scanning calorimeter ("DSC-7" available from Perkin Elmer Co., Ltd.) as follows. Namely, 10 mg of a sample is melted at 230°C for 3 minutes in a nitrogen atmosphere, and then cooled up to 0°C at a temperature drop rate of 10°C/minute. The crystallization exotherm curve was prepared through the above procedure. The peak top of maximum peak observed in the thus prepared crystallization exotherm curve was determined to be a crystallization temperature  $T_c$  (°C) of the sample. Further, the sample is held at 0°C for 3 minutes, and then heated at a temperature rise rate of 10°C/minute, thereby preparing a melting endotherm curve. The peak top of a maximum peak observed in the thus prepared melting endotherm curve is determined to be the melting temperature  $T_m$ .

$$[(m-2,1) + (r-2,1) + (1,3)] \leq 5.0\% \quad (1)$$

wherein (m-2,1) is a content (%) of 2,1-meso insertion as measured by <sup>13</sup>C-NMR; (r-2,1) is a content (%) of 2,1-racemic insertion as measured by

$^{13}\text{C}$ -NMR; and (1,3) is a content (%) of 1,3-insertion as measured by

$^{13}\text{C}$ -NMR,

more preferably satisfies the following formula (2):

$$[(m-2,1) + (r-2,1) + (1,3)] \leq 1.0\% \quad (2), \text{ and}$$

most preferably satisfies the following formula (3):

$$[(m-2,1) + (r-2,1) + (1,3)] \leq 0.1\% \quad (3).$$

The polymer incapable of satisfying the formula (1) is deteriorated in crystallinity beyond expectation, resulting in increased stickiness.

The insertion contents (m-2,1), (r-2,1) and (1,3) are calculated from integrated intensities of respective peaks in  $^{13}\text{C}$ -NMR spectra which are determined to be attributed to the respective insertions according to the method reported in Grassi, et al., "Macromolecules", No. 21, p. 617 (1988) and Busico, et al., "Macromolecules", No. 27, p. 7538 (1994). Specifically, the content (m-2,1) is a 2,1-meso insertion content (%) calculated from a ratio of an integrated intensity of peak attributed to  $P\alpha$ ,  $\gamma$  threo observed near 17.2 ppm to that of a whole methyl carbon region. The content (r-2,1) is a 2,1-racemic insertion content (%) calculated from a ratio of an integrated intensity of peak attributed to  $P\alpha$ ,  $\gamma$  threo observed near 15.0 ppm to that of a whole methyl carbon region. The content (1,3) is a 1,3-insertion content (%) calculated from a ratio of an integrated intensity of peak attributed to  $T\beta$ ,  $\gamma+$  observed near 31.0 ppm to that of a whole methyl carbon region.

Further, the propylene homopolymer of the present invention more preferably shows substantially no peak attributed to a molecular chain end (n-butyl) derived from the 2,1-insertion upon  $^{13}\text{C}$ -NMR spectra measurement. With respect to the molecular chain end derived from the 2,1-insertion, the respective insertion contents are calculated from integrated intensities of peaks in  $^{13}\text{C}$ -NMR spectra which are determined to be attributed to the respective insertions according to the method reported in Jungling, et al., "J. Polym. Sci.: Part A: Polym. Chem.", No. 33, p. 1305 (1995). Meanwhile, in the case of isotactic polypropylene, the peak appearing near 18.9 ppm is attributed to the end methyl carbon of n-butyl. The  $^{13}\text{C}$ -NMR spectra measurements of the abnormal insertion and the

molecular chain end may be performed by using the same apparatus and conditions as described above.

Still further, the propylene homopolymer of the present invention preferably contains a fraction extracted with boiling diethyl ether, as an index of elastic modulus, in an amount of 5 wt% or more. The fraction extracted with boiling dimethyl ether is measured using a Soxhlet extractor under the following conditions:

Sample amount: 1-2 g;

Sample form: powder (pelletized sample was powdered by pulverization);

Extractant: diethyl ether;

Extraction time: 10 hours;

Extraction frequency: 180 times or more; and

Calculation method: calculated from the following equation:

[Amount of a fraction extracted with diethyl ether (g) /weight of powder charged (g)] x 100.

In addition to the above, the tensile modulus of the propylene homopolymer of the present invention is preferably 100 MPa or lower, more preferably 70 MPa or lower. The tensile modulus of the propylene homopolymer is preferably 6 MPa or higher. When the tensile modulus of the propylene homopolymer is less than 6 MPa, the molded product obtained from such a propylene homopolymer tends to be deteriorated in shape retentivity.

[a'] Propylene copolymer

The propylene copolymer of the present invention is a copolymer produced by copolymerizing propylene with ethylene and/or a C<sub>4</sub>-C<sub>20</sub> α-olefin, and satisfies the following requirements of (1) and (2):

- (1) a stereoregularity index (P) of 55-90 mol% as determined by  $^{13}\text{C}$ -NMR measurement; and
- (2) a fraction (W25) eluted at a temperatures up to 25°C by temperature-programmed chromatography, of from 20-100 wt%.

The propylene copolymer satisfying the above requirements enables the production of a molded product that is well-balanced between an amount

of sticky components, elastic modulus and transparency. That is, the obtained molded product has a low elastic modulus, excellent softness (also referred to as flexibility), less stickiness, good surface properties (typified by less bleeding of sticky components, less migration of sticky components to other articles and the like) and excellent transparency. The stereoregularity index (P) is determined based on a meso triad fraction [mm] in propylene chains in  $^{13}\text{C}$ -NMR spectra as measured using an NMR spectrometer "JNM-EX400 Model" available from Nippon Denshi Co., Ltd. under the same conditions as described above. The larger value of P means higher stereoregularity of the copolymer. The stereoregularity index (P) of the propylene copolymer of the present invention is more preferably from 65 to 80 mol%. When the stereoregularity index (P) is less than 55 mol%, the copolymer has poor moldability due to deteriorated elastic modulus. When the stereoregularity index (P) exceeds 90 mol%, the copolymer tends to become hard. The W25 value of the propylene copolymer is preferably 30 to 100 wt%, more preferably 50 to 100 wt%. When the W25 is less than 20 wt%, the propylene copolymer fails to show a good flexibility. Meanwhile, the definition and the measuring method for W25 of the propylene copolymer are the same as described above.

In addition to the above requirements, the propylene copolymer of the present invention preferably has a molecular weight distribution (Mw/Mn) of 4 or less as measured by gel permeation chromatography (GPC), and/or an intrinsic viscosity  $[\eta]$  of 0.5 to 15.0 dl/g as measured at 135°C in tetralin. More preferably, the Mw/Mn is 3.5 or less and/or the  $[\eta]$  is 1.0-5.0 dl/g, and still more preferably, the Mw/Mn is 3 or less and/or the  $[\eta]$  is 1.0-3.0 dl/g. When the molecular weight distribution (Mw/Mn) exceeds 4, the resulting polymer tends to become sticky. When the intrinsic viscosity  $[\eta]$  is less than 0.5 dl/g, the resulting polymer also tends to become sticky. When the intrinsic viscosity  $[\eta]$  exceeds 15.0 dl/g, the resulting polymer has poor moldability due to deteriorated fluidity. Meanwhile, the measuring method for the Mw/Mn of the propylene copolymer is the same as described above.

In addition to the above requirements, the propylene copolymer of the present invention preferably has a melting endotherm  $\Delta H$  of 20 J/g or lower

as measured by DSC for excellent flexibility. Further, the propylene copolymer may or may not have a melting temperature ( $T_m$ ) and a crystallization temperature ( $T_c$ ). From the standpoint of flexibility, it is preferable that the propylene copolymer has either no  $T_m$  and  $T_c$  or low  $T_m$  and  $T_c$ . More specifically, the  $T_m$  is, if measurable, preferably 100°C or lower. Meanwhile, the measuring methods for the  $\Delta H$ ,  $T_m$  and  $T_c$  of the propylene copolymer are the same as described above.

Further, in addition to the above requirements, the propylene copolymer preferably contains a fraction extracted with boiling diethyl ether, as an index of elastic modulus, in an amount of 5 wt% or more. Meanwhile, the method for measuring the fraction extracted with boiling diethyl ether is the same as described above.

Furthermore, the tensile modulus of the propylene copolymer is preferably 100 MPa or lower, more preferably 70 MPa or lower. The tensile modulus of the propylene copolymer is preferably 6 MPa or higher. When the tensile modulus of the propylene copolymer is less than 6 MPa, the molded product obtained from such a propylene copolymer tends to be deteriorated in shape retentivity.

Examples of the  $C_4$ - $C_{20}$   $\alpha$ -olefins used for producing the propylene copolymer of the present invention, include ethylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicocene or the like. In the present invention, these olefins may be used alone or in the form of a mixture of any two or more thereof.

Also, the propylene copolymer is preferably a random copolymer containing structural units resulting from propylene in an amount of preferably 90 mol% or more, more preferably 95 mol% or more.

[Production methods of propylene homopolymer (a) and propylene copolymer (a')]

The propylene homopolymer (a) and the propylene copolymer (a') of the present invention are respectively produced by homopolymerizing propylene and by copolymerizing propylene with ethylene and/or a  $C_4$ - $C_{20}$   $\alpha$ -olefin, in the presence of a so-called metallocene catalyst. Examples of the



or different, and may be cross-linked with the other X group, E<sup>1</sup>, E<sup>2</sup> or Y;

Y is a Lewis base with the proviso that when a plurality of Y groups are present, these groups may be same or different, and may be cross-linked with the other Y group, E<sup>1</sup>, E<sup>2</sup> or X;

A<sup>1</sup> and A<sup>2</sup> are divalent cross-linking groups capable of bonding the two ligands E<sup>1</sup> and E<sup>2</sup> to each other, are respectively a C<sub>1</sub>-C<sub>20</sub> hydrocarbon group, a C<sub>1</sub>-C<sub>20</sub> halogen-containing hydrocarbon group, a silicon-containing group, a germanium-containing group, a tin-containing group, -O-, -CO-, -S-, -SO<sub>2</sub>-, -Se-, -NR<sup>1</sup>-, -PR<sup>1</sup>-, -P(O)R<sup>1</sup>-, -BR<sup>1</sup>- or -AlR<sup>1</sup>- wherein R<sup>1</sup> is a hydrogen atom, a halogen atom, a C<sub>1</sub>-C<sub>20</sub> hydrocarbon group or a C<sub>1</sub>-C<sub>20</sub> halogen-containing hydrocarbon group, and may be the same or different;

q is an integer of 1 to 5 given by the formula:

[(valence of M) - 2]; and

r is an integer of 0 to 3, and

(B) a component selected from the group consisting of (B-1) a compound capable of forming an ionic complex by reacting with the transition metal compound (A) or a derivative thereof, (B-2) aluminoxane, and (B-3) a Lewis acid.

In the above general formula (I), M represents a metal element belonging to Groups 3 to 10 of the Period Table or lanthanoid series. Specific examples of the metal elements include titanium, zirconium, hafnium, yttrium, vanadium, chromium, manganese, nickel, cobalt, palladium and lanthanoid series metals. Of these, titanium, zirconium and hafnium are preferred from the standpoint of olefin polymerization activity and so forth. E<sup>1</sup> and E<sup>2</sup> respectively represent a ligand selected from the group consisting of a substituted cyclopentadienyl group, indenyl group, substituted indenyl group, heterocyclopentadienyl group, substituted heterocyclopentadienyl group, amide group (-N<), phosphide group (-P<), hydrocarbon group (>CR-, >C<) and silicon-containing group (>SiR-, >Si<) (where, R is hydrogen, a C<sub>1</sub>-C<sub>20</sub> hydrocarbon group or a heteroatom-containing group), and they form a crosslinked structure via A<sup>1</sup> and A<sup>2</sup>. In addition, E<sup>1</sup> and E<sup>2</sup> may be the same or different. Preferable examples of E<sup>1</sup> and E<sup>2</sup> include substituted cyclopentadienyl groups, indenyl

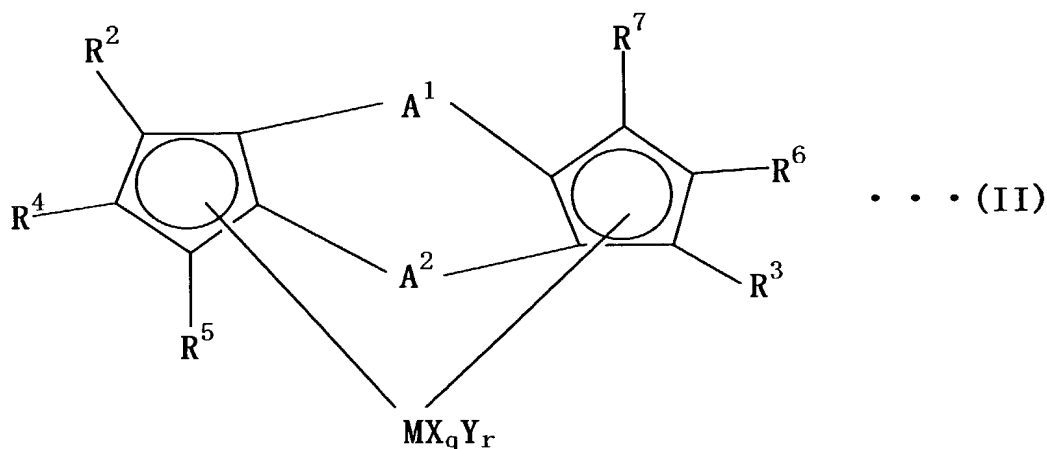
groups and substituted indenyl groups.

In addition, X represents a  $\sigma$ -bonding or  $\pi$ -bonding ligand, and in the case X is plural, the plurality of X may be the same or different, and they may be crosslinked with other X, E<sup>1</sup>, E<sup>2</sup> or Y. Specific examples of  $\sigma$ -bonding ligands include a halogen atom, a C<sub>1</sub>-C<sub>20</sub> hydrocarbon group, an C<sub>1</sub>-C<sub>20</sub> alkoxy group, an C<sub>6</sub>-C<sub>20</sub> aryloxy group, a C<sub>1</sub>-C<sub>20</sub> amide group, a C<sub>1</sub>-C<sub>20</sub> silicon-containing group, a C<sub>1</sub>-C<sub>20</sub> phosphide group, a C<sub>1</sub>-C<sub>20</sub> sulfide group, a C<sub>1</sub>-C<sub>20</sub> sulfoxide group and a C<sub>1</sub>-C<sub>20</sub> acyl group. Examples of halogen atoms include a chlorine atom, a fluorine atom, a bromine atom and an iodine atom. Specific examples of C<sub>1</sub>-C<sub>20</sub> hydrocarbon groups include alkyl groups such as a methyl group, ethyl group, propyl group, butyl group, hexyl group, cyclohexyl group and octyl group; alkenyl groups such as a vinyl group, propenyl group and cyclohexenyl group; arylalkyl groups such as a benzyl group, phenylethyl group and phenylpropyl group; and aryl groups such as a phenyl group, tolyl group, dimethylphenyl group, trimethylphenyl group, ethylphenyl group, propylphenyl group, biphenyl group, naphthyl group, methylnaphthyl group, anthracenyl group and phenanthrenyl group. Among these, alkyl groups such as a methyl group, ethyl group or propyl group, and aryl groups such as a phenyl group are particularly preferable. Examples of C<sub>1</sub>-C<sub>20</sub> halogenated hydrocarbon groups include halogenated hydrocarbon groups in which the above hydrocarbon groups are substituted with a halogen atom. Among these, halogenated alkyl groups such as a trifluoromethyl group and trichloromethyl group are particularly preferable. Examples of C<sub>1</sub>-C<sub>20</sub> alkoxy groups include alkoxy groups such as a methoxy group, ethoxy group, propoxy group and butoxy group, a phenylmethoxy group and a phenylethoxy group. Examples of C<sub>6</sub>-C<sub>20</sub> aryloxy groups include a phenoxy group, methylphenoxy group and dimethylphenoxy group. Examples of C<sub>1</sub>-C<sub>20</sub> amide groups include alkylamide groups such as a dimethylamide group, diethylamide group, dipropylamide group, dibutylamide group, dicyclohexylamide group and methylethylamide group, and alkenylamide groups such as a divinylamide group, dipropenylamide group and dicyclohexenylamide group; arylalkylamide groups such as a dibenzylamide

group, phenylethylamide group and phenylpropylamide group; and, arylamide groups such as a diphenylamide and dinaphthylamide group. Examples of  $C_1$ - $C_{20}$  silicon-containing groups include mono-hydrocarbon-substituted silyl groups such as a methylsilyl group and phenylsilyl group; di-hydrocarbon-substituted silyl groups such as a dimethylsilyl group and diphenylsilyl group; tri-hydrocarbon-substituted silyl groups such as a trimethylsilyl group, triethylsilyl group, tripropylsilyl group, tricyclohexylsilyl group, triphenylsilyl group, dimethylphenylsilyl group, methyldiphenylsilyl group, tritolylsilyl group and trinaphthylsilyl group; hydrocarbon-substituted silyl ether groups such as a trimethylsilyl ether group; silicon-substituted alkyl groups such as a trimethylsilylmethyl group and phenyldimethylsilylethyl group; and, silicon-substituted aryl groups such as a trimethylsilylphenyl group. Among these, silicon-substituted alkyl group is preferable and a trimethylsilylmethyl group, phenyldimethylsilylethyl group and so forth are particularly preferable. Examples of  $C_1$ - $C_{20}$  sulfide groups include alkylsulfide groups such as a methylsulfide group, ethylsulfide group, propylsulfide group, butylsulfide group, hexylsulfide group, cyclohexylsulfide group and octylsulfide group, alkenylsulfide groups such as a vinylsulfide group, propenylsulfide group and cyclohexenylsulfide group; arylalkylsulfide groups such as a benzylsulfide group, phenylethylsulfide group and phenylpropylsulfide group; and arylsulfide groups such as a phenylsulfide group, tolylsulfide group, dimethylphenylsulfide group, trimethylphenylsulfide group, ethylphenylsulfide group, propylphenylsulfide group, biphenylsulfide group, naphthylsulfide group, methylnaphthylsulfide group, anthracenylsulfide group and phenanthrenylsulfide group. Examples of  $C_1$ - $C_{20}$  sulfoxide groups include alkylsulfoxide groups such as a methylsulfoxide group, ethylsulfoxide group, propylsulfoxide group, butylsulfoxide group, hexylsulfoxide group, cyclohexylsulfoxide group and octylsulfoxide group, alkenylsulfoxide groups such as a vinylsulfoxide group, propenylsulfoxide group and cyclohexenylsulfoxide group; arylalkylsulfoxide groups such as a benzylsulfoxide group, phenylethylsulfoxide group and







are preferable.

In the above general formula (II), M, X, Y, A<sup>1</sup>, A<sup>2</sup>, q and r are the same as defined in the above general formula (I). Although R<sup>2</sup> through R<sup>7</sup> respectively indicate a hydrogen atom, halogen atom, C<sub>1</sub>-C<sub>20</sub> hydrocarbon group, C<sub>1</sub>-C<sub>20</sub> halogen-containing hydrocarbon group, silicon-containing group or heteroatom-containing group, it is necessary that at least one of those groups not be a hydrogen atom, and preferably is a group that contains a heteroatom such as oxygen, halogen or silicon. In addition, R<sup>2</sup> through R<sup>7</sup> may be mutually the same or different, and may form a ring by mutually bonding of adjacent groups. In particular, it is preferable that R<sup>4</sup> and R<sup>5</sup> form a ring and that R<sup>6</sup> and R<sup>7</sup> form a ring. Preferable examples of R<sup>2</sup> and R<sup>3</sup> include groups that contain a heteroatom such as oxygen, halogen or silicon because of their high polymerization activity. The transition metal compounds represented by general formula (II) are preferable for the transition metal compounds represented by general formula (I), and among the transition metal compounds represented by general formula (II), those in which R<sup>2</sup> through R<sup>7</sup> are groups that contain a heteroatom are preferable. A transition metal compound represented by general formula (III) is the most preferable.

The transition metal compound having a double-crosslinkedbiscyclopentadienyl derivative for its ligand is preferably that in which the ligand is of the (1,2')(2,1') double-crosslinked type.

Specific examples of a transition metal compound represented by

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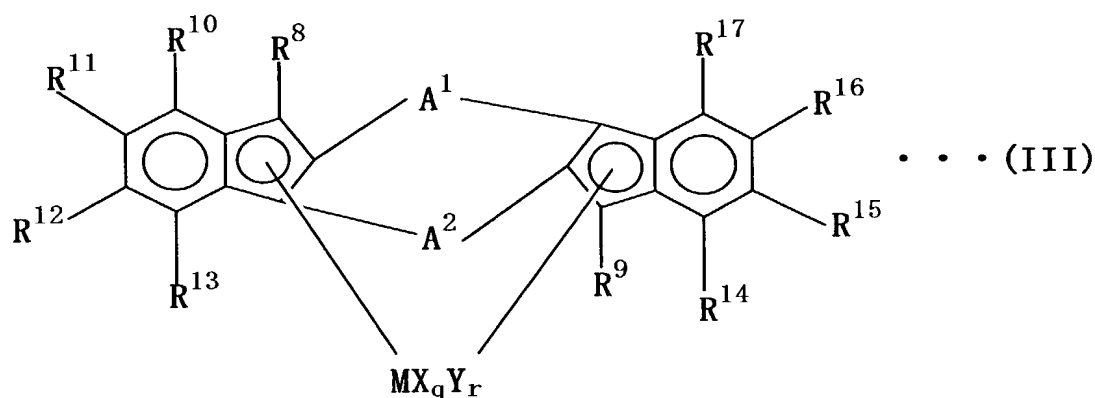
di-i-propylindenyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(4-phenylindenyl)zirconium  
 dichloride,  
 (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-methyl-4-i-propylindenyl)  
 zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(5,6-benzoindenyl)zirconium  
 dichloride, (1,2'-dimethylsilylene)(2,1'-isopropylidene)bis(indenyl)zirconium  
 dichloride,  
 (1,2'-dimethylsilylene)(2,1'-isopropylidene)bis(3-methylindenyl)zirconium  
 dichloride,  
 (1,2'-dimethylsilylene)(2,1'-isopropylidene)bis(3-i-propylindenyl)zirconium  
 dichloride,  
 (1,2'-dimethylsilylene)(2,1'-isopropylidene)bis(3-n-butylindenyl)zirconium  
 dichloride,  
 (1,2'-dimethylsilylene)(2,1'-isopropylidene)bis(3-trimethylsilylmethylindenyl  
 )zirconium dichloride, (1,2'-dimethylsilylene)(2,1'-isopropylidene)bis(3-  
 trimethylsilylindenyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-isopropylidene)bis(3-phenylindenyl)zirconium  
 dichloride, (1,2'-dimethylsilylene)(2,1'-methylene)bis(indenyl)zirconium  
 dichloride,  
 (1,2'-dimethylsilylene)(2,1'-methylene)bis(3-methylindenyl)zirconium  
 dichloride, (1,2'-dimethylsilylene)(2,1'-methylene)bis(3-i-propylindenyl)  
 zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-methylene)bis(3-n-butylindenyl)zirconium  
 dichloride, (1,2'-ethylene)(2,1'-methylene)(3-methyl  
 cyclopentadienyl)(3'-methyl cyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-methylene)bis(3-  
 trimethylsilylmethylindenyl)zirconium dichloride,  
 (1,2'-diphenylsilylene)(2,1'-methylene)bis(indenyl)zirconium dichloride,  
 (1,2'-diphenylsilylene)(2,1'-methylene)bis(3-methylindenyl)zirconium  
 dichloride,  
 (1,2'-diphenylsilylene)(2,1'-methylene)bis(3-i-propylindenyl)zirconium  
 dichloride, (1,2'-diphenylsilylene)(2,1'-methylene)bis(3-n-butylindenyl)

zirconium dichloride, (1,2'-diphenylsilylene)(2,1'-methylene)bis(3-trimethylsilylmethylindenyl)zirconium dichloride, (1,2'-diphenylsilylene)(2,1'-methylene)bis(3-trimethylsilylindenyl)zirconium dichloride, (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)(3-methylcyclopentadienyl)(3'-methylcyclopentadienyl)zirconium dichloride, (1,2'-dimethylsilylene)(2,1'-isopropylidene)(3-methylcyclopentadienyl)(3'-methylcyclopentadienyl)zirconium dichloride, (1,2'-dimethylsilylene)(2,1'-ethylene)(3-methylcyclopentadienyl)(3'-methylcyclopentadienyl)zirconium dichloride, (1,2'-ethylene)(2,1'-isopropylidene)(3-methylcyclopentadienyl)(3'-methylcyclopentadienyl)zirconium dichloride, (1,2'-methylene)(2,1'-methylene)(3-methylcyclopentadienyl)(3'-methylcyclopentadienyl)zirconium dichloride, (1,2'-methylene)(2,1'-isopropylidene)(3-methylcyclopentadienyl)(3'-methylcyclopentadienyl)zirconium dichloride, (1,2'-isopropylidene)(2,1'-isopropylidene)(3-methylcyclopentadienyl)(3'-methylcyclopentadienyl)zirconium dichloride, (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)(3,4-dimethylcyclopentadienyl)(3',4'-dimethylcyclopentadienyl)zirconium dichloride, (1,2'-dimethylsilylene)(2,1'-isopropylidene)(3,4-dimethylcyclopentadienyl)(3',4'-dimethylcyclopentadienyl)zirconium dichloride, (1,2'-dimethylsilylene)(2,1'-ethylene)(3,4-dimethylcyclopentadienyl)(3',4'-dimethylcyclopentadienyl)zirconium dichloride, (1,2'-ethylene)(2,1'-methylene)(3,4-dimethylcyclopentadienyl)(3',4'-dimethylcyclopentadienyl)zirconium dichloride, (1,2'-ethylene)(2,1'-isopropylidene)(3,4-dimethylcyclopentadienyl)(3',4'-dimethylcyclopentadienyl)zirconium dichloride, (1,2'-methylene)(2,1'-methylene)(3,4-dimethylcyclopentadienyl)(3',4'-dimethylcyclopentadienyl)zirconium dichloride, (1,2'-methylene)(2,1'-isopropylidene)(3,4-dimethylcyclopentadienyl)(3',4'-dimethylcyclopentadienyl)zirconium dichloride, (1,2'-isopropylidene)(2,1'-isopropylidene)(3,4-dimethylcyclopentadienyl)

(3',4'-dimethylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)(3-methyl-5-ethylcyclopentadienyl)(3'-methyl-5'-ethylcyclopentadienyl) zirconium dichloride, (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)(3-methyl-5-isopropylcyclopentadienyl)(3'-methyl-5'-isopropylcyclopentadienyl)zirconium dichloride, (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)(3-methyl-5-n-butylcyclopentadienyl)(3'-methyl-5'-n-butylcyclopentadienyl)zirconium dichloride, (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)(3-methyl-5-phenylcyclopentadienyl)(3'-methyl-5'-phenylcyclopentadienyl)zirconium dichloride, (1,2'-dimethylsilylene)(2,1'-isopropylidene)(3-methyl-5-ethylcyclopentadienyl)(3'-methyl-5'-ethylcyclopentadienyl) zirconium dichloride, (1,2'-dimethylsilylene)(2,1'-isopropylidene)(3-methyl-5-i-propylcyclopentadienyl)(3'-methyl-5'-i-propylcyclopentadienyl)zirconium dichloride, (1,2'-dimethylsilylene)(2,1'-isopropylidene)(3-methyl-5-n-butylcyclopentadienyl)(3'-methyl-5'-n-butylcyclopentadienyl)zirconium dichloride, (1,2'-dimethylsilylene)(2,1'-isopropylidene)(3-methyl-5-phenylcyclopentadienyl)(3'-methyl-5'-phenylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-ethylene)(3-methyl-5-ethylcyclopentadienyl)(3'-methyl-5'-ethylcyclopentadienyl) zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-ethylene)(3-methyl-5-i-propylcyclopentadienyl)(3'-methyl-5'-i-propylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-ethylene)(3-methyl-5-n-butylcyclopentadienyl)(3'-methyl-5'-n-butylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-ethylene)(3-methyl-5-phenylcyclopentadienyl)(3'-methyl-5'-phenylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-methylene)(3-methyl-5-ethylcyclopentadienyl)(3'-methyl-5'-ethylcyclopentadienyl) zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-methylene)(3-methyl-5-i-propylcyclopentadienyl)(3'-methyl-5'-i-propylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-methylene)(3-methyl-5-n-butylcyclopentadienyl)(3'-methyl-5'-n-butylcyclopentadienyl)zirconium dichloride,  
 (1,2'-dimethylsilylene)(2,1'-methylene)(3-methyl-5-phenylcyclopentadienyl)(3'-methyl-5'-phenylcyclopentadienyl)zirconium dichloride,

(3'-methyl-5'-phenylcyclopentadienyl)zirconium dichloride,  
 (1,2'-ethylene)(2,1'-methylene)(3-methyl-5-i-propylcyclopentadienyl)(3'-methyl-5'-i-pentacyclopentadienyl)zirconium dichloride,  
 (1,2'-ethylene)(2,1'-isopropylidene)(3-methyl-5-i-propylcyclopentadienyl)(3'-methyl-5'-i-propylcyclopentadienyl)zirconium dichloride,  
 (1,2'-methylene)(2,1'-methylene)(3-methyl-5-i-propylcyclopentadienyl)(3'-methyl-5'-i-propylcyclopentadienyl)zirconium dichloride,  
 (1,2'-methylene)(2,1'-isopropylidene)(3-methyl-5-i-propylcyclopentadienyl)(3'-methyl-5'-i-propylcyclopentadienyl)zirconium dichloride, and those in which the zirconium in these compounds is substituted with titanium or hafnium. Naturally, the transition metal compound represented by general formula (I) is not limited to these examples. In addition, the transition metal compound represented by general formula (I) may also be a similar compound of a metal element of another group or member of the Lanthanoid series.

Among the transition metal compounds represented by the above general formula (II), transition metal compounds represented by general formula (III):



are preferable.

In the above general formula (III), M, X, Y, A<sup>1</sup>, A<sup>2</sup>, q and r are the same as defined in the above general formula (I). At least one of R<sup>8</sup> and R<sup>9</sup> indicate a group containing a heteroatom such as oxygen, halogen or silicon, and R<sup>10</sup> through R<sup>17</sup> indicate hydrogen atoms, C<sub>1</sub>-C<sub>20</sub> hydrocarbon groups or groups containing a heteroatom such as oxygen, halogen or silicon.

Specific examples of transition metal compounds represented by the above general formula (III) include

(1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-trimethylsilylmethylindenyl)zirconium dichloride,  
(1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-ethoxymethylindenyl)zirconium dichloride,  
(1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-ethoxyethylindenyl)zirconium dichloride,  
(1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-methoxymethylindenyl)zirconium dichloride,  
(1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-methoxyethylindenyl)zirconium dichloride,  
(1,2'-dimethylsilylene)(2,1'-isopropylidene)bis(3-trimethylsilylmethylindenyl)zirconium dichloride,  
(1,2'-dimethylsilylene)(2,1'-isopropylidene)bis(3-trimethylsilylindenyl)zirconium dichloride,  
(1,2'-dimethylsilylene)(2,1'-methylene)bis(3-



hydrogen atom,  $C_1$ - $C_{20}$  alkyl group, or an aryl group,  $C_6$ - $C_{20}$  alkylaryl group or arylalkyl group;  $R^{31}$  and  $R^{32}$  respectively indicate a cyclopentadienyl group, substituted cyclopentadienyl group, indenyl group or fluorenyl group;  $R^{33}$  indicates an  $C_1$ - $C_{20}$  alkyl group, aryl group, alkylaryl group or arylalkyl group;  $R^{34}$  indicates a large ring ligand such as tetraphenylporphyrin and phthalocyanine;  $k$  indicates an integer of 1 to 3 that is the ionization number of  $[L^1-R^{30}]$ ,  $[L^2]$ ;  $a$  is an integer of 1 or more;  $b = (k \times a)$ ;  $M^2$  includes an element from groups 1-3, 11-13 or 17 of the periodic table; and,  $M^3$  indicates an element of groups 7-12 of the periodic table].

Here, specific examples of  $L^1$  include amines such as ammonia, methylamine, aniline, dimethylamine, diethylamine, *N*-methylaniline, diphenylamine, *N,N*-dimethylaniline, trimethylamine, triethylamine, tri-*n*-butylamine, methyldiphenylamine, pyridine, *p*-bromo-*N,N*-dimethylaniline and *p*-nitro-*N,N*-dimethylaniline; phosphines such as triethylphosphine, triphenylphosphine and diphenylphosphine; thioethers such as tetrahydrothiophene; esters such as ethylbenzoate; and nitriles such as acetonitrile and benzonitrile.

Specific examples of  $R^{30}$  include hydrogen, a methyl group, ethyl group, benzyl group and trityl group, while specific examples of  $R^{31}$  and  $R^{32}$  include a cyclopentadienyl group, methylcyclopentadienyl group, ethylcyclopentadienyl group and pentamethylcyclopentadienyl group. Specific examples of  $R^{33}$  include a phenyl group, *p*-tolyl group and *p*-methoxyphenyl group, while examples of  $R^{34}$  include tetraphenylporphyrin, phthalocyanine, allyl and methallyl. In addition, specific examples of  $M^2$  include Li, Na, K, Ag, Cu, Br, I and  $I_3$ , while specific examples of  $M^3$  include Mn, Fe, Co, Ni and Zn.

In addition, in  $[Z^1]^-$ , namely  $[M^1G^1G^2...G^f]$ , specific examples of  $M^1$  include B, Al, Si, P, As and Sb, and preferably include B and Al. In addition, specific examples of  $G^1$ ,  $G^2$  through  $G^f$  include dialkylamino groups such as a dimethylamino group and diethylamino group, alkoxy or aryloxy groups such as a methoxy group, ethoxy group, *n*-butoxy group and phenoxy group, hydrocarbon groups such as a methyl group, ethyl group, *n*-propyl group, isopropyl group, *n*-butyl group, isobutyl group, *n*-octyl group,

n-eicosyl group, phenyl group, p-tolyl group, benzyl group, 4-t-butylphenyl group and 3,5-dimethylphenyl group, halogen atoms such as fluorine, chlorine, bromine and iodine, heteroatom-containing hydrocarbon groups such as a p-fluorophenyl group, 3,5-difluorophenyl group, pentachlorophenyl group, 3,4,5-trifluorophenyl group, pentafluorophenyl group, 3,5-bis(trifluoromethyl)phenyl group and bis(trimethylsilyl)methyl group, and organic metalloid groups such as a pentamethyl antimony group, trimethylsilyl group, trimethylgermyl group, diphenylarsine group, dicyclohexylantimony group and diphenylboron.

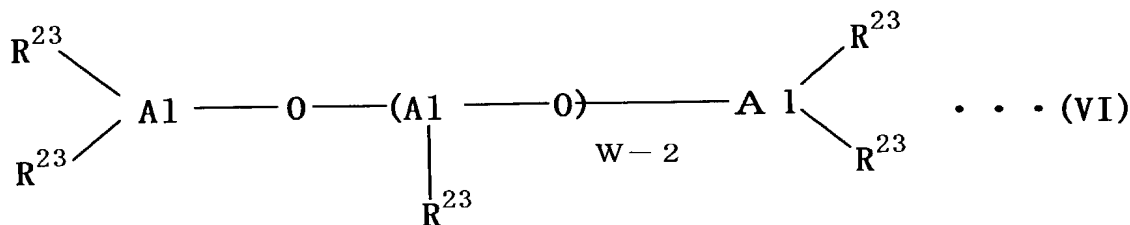
In addition, specific examples of a non-coordinating anion, namely conjugate base  $[Z^2]^-$  of a Bronsted acid alone or the combination of a Bronsted acid and Lewis acid, having a  $pK_a$  of -10 or less, include trifluoromethanesulfonate anion  $(CF_3SO_3)^-$ , bis(trifluoromethanesulfonyl)methyl anion, bis(trifluoromethanesulfonyl)benzyl anion, bis(trifluoromethanesulfonyl)amide, perchlorate anion  $(ClO_4)^-$ , trifluoroacetate anion  $(CF_3CO_2)^-$ , hexafluoroantimony anion  $(SbF_4)^-$ , fluorosulfonate anion  $(FSO_3)^-$ , chlorosulfonate anion  $(ClSO_3)^-$ , fluorosulfonate anion/5-antimony fluoride  $(FSO_3/SbF_5)^-$ , fluorosulfonate anion/5-boron fluoride  $(FSO_3/AsF_5)^-$ , and trifluoromethanesulfonate 5-antimony fluoride  $(CF_3SO_3/SbF_5)^-$ .

Specific examples of ionic compounds that form an ionic complex by reacting with the transition metal compound of the above component (A), namely compounds of component (B-1), include tetraphenylborate triethylammonium, tetraphenylborate tri-n-butylammonium, tetraphenylborate trimethylammonium, tetraphenylborate tetraethylammonium, tetraphenylborate methyl (tri-n-butyl)ammonium, tetraphenylborate benzyl(tri-n-butyl)ammonium, tetraphenylborate dimethyldiphenylammonium, tetraphenylborate triphenyl(methyl)ammonium, tetraphenylborate trimethylanilinium, tetraphenylborate methylpyridinium, tetraphenylborate benzylpyridinium, tetraphenylborate methyl(2-cyanopyridinium), tetrakis(pentafluorophenyl) borate triethylammonium, tetrakis(pentafluorophenyl)borate

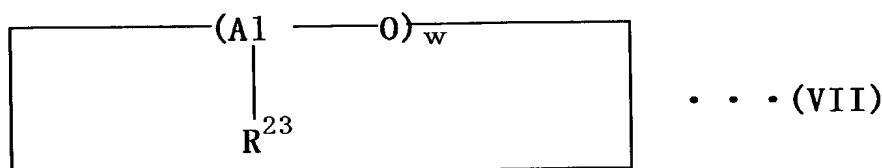
tri-n-butylammonium, tetrakis(pentafluorophenyl)borate  
 triphenylammonium, tetrakis(pentafluorophenyl)borate  
 tetra-n-butylammonium, tetrakis(pentafluorophenyl)borate  
 tetraethylammonium, tetrakis(pentafluorophenyl)borate  
 benzyl(tri-n-butyl)ammonium, tetrakis(pentafluorophenyl) borate  
 methyldiphenylammonium, tetrakis(pentafluorophenyl) borate  
 triphenyl(methyl)ammonium, tetrakis(pentafluorophenyl)borate  
 methylanilinium, tetrakis(pentafluorophenyl)borate dimethylanilinium,  
 tetrakis(pentafluorophenyl)borate trimethylanilinium,  
 tetrakis(pentafluorophenyl)borate methylpyridinium,  
 tetrakis(pentafluorophenyl)borate benzylpyridinium,  
 tetrakis(pentafluorophenyl)borate methyl(2-cyanopyridinium),  
 tetrakis(pentafluorophenyl)borate benzyl(2-cyanopyridinium),  
 tetrakis(pentafluorophenyl) borate methyl(4-cyanopyridinium),  
 tetrakis(pentafluorophenyl)borate triphenylphosphonium,  
 tetrakis[bis(3,5-ditrifluoromethyl)phenyl]borate dimethylanilinium,  
 tetraphenylborate ferrocenium, silver tetraphenylborate, trityl  
 tetraphenylborate, tetraphenylborate tetraphenylporphyrin manganese,  
 tetrakis(pentafluorophenyl)borate ferrocenium,  
 tetrakis(pentafluorophenyl)borate (1,1'-dimethylferrocenium),  
 tetrakis(pentafluorophenyl)borate decamethylferrocenium, silver  
 tetrakis(pentafluorophenyl) borate, trityl tetrakis(pentafluorophenyl)borate,  
 lithium tetrakis(pentafluorophenyl)borate, sodium  
 tetrakis(pentafluorophenyl)borate, tetrakis(pentafluorophenyl)borate  
 tetraphenylporphyrin manganese, silver tetrafluoroborate, silver  
 hexafluorophosphate, silver hexafluoroarsenate, silver perchlorate, silver  
 trifluoroacetate and silver trifluoromethanesulfonate.

One type of (B-1) or a combination of two or more types may be used.

On the other hand, examples of the aluminoxane of component (B-2) include the linear aluminoxane represented by general formula (VI):



(wherein,  $\text{R}^{23}$  indicates a hydrocarbon group such as a  $\text{C}_1$ - $\text{C}_{20}$ , preferably  $\text{C}_1$ - $\text{C}_{12}$  alkyl group, alkenyl group, aryl group or arylalkyl group, or a halogen atom,  $w$  indicates the mean degree of polymerization, and is normally an integer from 2 to 50, and preferably an integer from 2 to 40, and each  $\text{R}^{23}$  may be the same or different), and the cyclic aluminosiloxane represented by general formula (VII):



(wherein,  $\text{R}^{23}$  and  $w$  are the same as defined in the above general formula (VI)).

Although an example of the production method of the above aluminosiloxane includes a method wherein aluminosiloxane is brought in contact with a condensing agent such as water, there are no particular restrictions on the means for accomplishing this, and they may be reacted in accordance with known methods. Examples of such methods include (1) a method in which an organic aluminum compound is dissolved in an organic solvent and then brought in contact with water, (2) a method in which an organic aluminum compound is initially added during polymerization followed by the addition of water, (3) a method in which crystalline water contained in a metal salt, etc. and adsorbed water of an inorganic compound and organic compound are reacted with an organic aluminum compound, and (4) a method in which trialkylaluminum is reacted with tetraalkyldialuminosiloxane followed by reacting with water. Furthermore, the aluminosiloxane may be insoluble in toluene.

One type or a combination of two or more types of these aluminosiloxanes may be used.

The ratio at which the above catalyst component (A) and catalyst component (B-3) are used is preferably a molar ratio of 10:1 to 1:2000, more preferably 5:1 to 1:1000, and most preferably 2:1 to 1:500. In the case of deviating from these ranges, the catalyst cost per unit weight of polymer increases, thereby making this impractical. In addition, components (B-1), (B-2) and (B-3) may be used alone or in a combination of two or more types for catalyst component (B).

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the case of deviating from the above range, the catalyst cost per unit weight of polymer increases, thus making this impractical. In addition, in the case of using compound (B-2), the molar ratio is preferably within the range of 1:1 to 1:1000000, and more preferably 1:10 to 1:10000. In the case of deviating from this range, catalyst cost per unit weight of polymer increases, thereby making this impractical. In addition, (B-1), (B-2) and (B-3) may be used along or in a combination of two or more types for catalyst component (B).

An organic aluminum compound in the form of component (C) can be used in addition to the above component (A) and component (B) for the polymerization catalyst in the production method of the present invention.

Here, a compound represented by general formula (VIII):



(wherein,  $R^{36}$  indicates a  $C_1$ - $C_{10}$  alkyl group, J indicates a hydrogen atom,  $C_1$ - $C_{20}$  alkoxy group,  $C_6$ - $C_{20}$  aryl group or halogen atom, and v is an integer of 1 to 3) is used for the organic aluminum compound of component (C).

Specific examples of compound represented by the above general formula (VIII) include trimethylaluminum, triethylaluminum, triisopropylaluminum, triisobutylaluminum, dimethylaluminum dichloride, diethylaluminum dichloride, methylaluminum dichloride, ethylaluminum dichloride, dimethylaluminum fluoride, diisobutylaluminum hydride, diethylaluminum hydride and ethylaluminum sesquidichloride.

One type or a combination of two or more types of these organic aluminum compounds may be used.

In the production method of the present invention, pre-contact can also be performed using the above component (A), component (B) and component (C). In the present invention, it is preferable to use component (A') and component (A'') for component (A). Although pre-contact can be performed by bringing, for example, component (B) in contact with component (A), there are no particular restrictions on this method, and any known method can be used. This pre-contact is effect for reducing production cost as a result of improving catalytic activity, reducing the proportion of (B) used that serves as an auxiliary catalyst and so forth. In addition, by



polystyrene, styrene-divinylbenzene copolymer, polyethylene, polypropylene, substituted polystyrene and polyarylate, as well as starch and carbon.

Preferable examples of carriers used in the present invention include  $\text{MgCl}_2$ ,  $\text{MgCl}(\text{OC}_2\text{H}_5)$ ,  $\text{Mg}(\text{OC}_2\text{H}_5)_2$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . Although varying according to the type and production method, the properties of the carrier are such that the mean particle size is normally 1-300  $\mu\text{m}$ , preferably 10-200  $\mu\text{m}$ , and more preferably 20-100  $\mu\text{m}$ .

If particle size is excessively small, the amount of fine particles in the polymer increases, while if the particle size is excessively large, the amount of coarse particles in the polymer increases, causing a decrease in bulk density and clogging of the hopper. In addition, the specific surface area of the carrier is normally 1-1000  $\text{m}^2/\text{g}$  and preferably 50-500  $\text{m}^2/\text{g}$ , while pore volume is normally 0.1-5  $\text{cm}^3/\text{g}$  and preferably 0.3-3  $\text{cm}^3/\text{g}$ .

If either specific surface area or pore volume deviates from the above ranges, catalyst activity may decrease. Furthermore, specific surface area and pore volume can be determined, for example, from the volume of nitrogen gas adsorbed in accordance with the BET method (see Journal of the American Chemical Society, Vol. 60, p. 309 (1938)).

Moreover, in the case the above carrier is an inorganic oxide, it is preferably used after baking normally at 150-1000°C and preferably at 200-800°C.

In the case at least one type of catalyst component is supported onto the above carrier, at least one of catalyst component (A) and catalyst component (B), and preferably both catalyst component (A) and catalyst component (B), are supported onto the above carrier.

Although there are no particular restrictions on the method for supporting at least one of component (A) and component (B) onto said carrier, examples of methods that can be used include: (1) a method in which at least one of component (A) and component (B) is mixed with carrier, (2) a method in which, after treating the carrier with an organic aluminum compound or halogen-containing silicon compound, at least one of component (A) and component (B) is mixed in an inert solvent, (3) a method in which a support is reacted with a mixture of component (A) and/or

In the present invention, when contacting the above components (A), (B) and (C), catalysis may be prepared by irradiating elastic wave. Examples of elastic waves include ordinary sound waves, a particularly preferable example of which is ultrasonic waves. More specifically, the elastic waves are ultrasonic waves having a frequency of 1-1000 kHz, and preferably 10-500 kHz.

In addition, in the present invention, a catalyst can be formed by performing the procedure of supporting at least one of component (A) and component (B) onto a carrier within the polymerization system. For example, a method can be used in which, after adding at least one of component (A) and component (B) and carrier, and further adding an organic aluminum compound of the above component (C) as necessary, an olefin such as ethylene is added at normal pressure to 2 MPa (gauge) to perform preliminary polymerization for about 1 minute to 2 hours at -20 to 200°C and form catalyst particles.

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within the above ranges. In addition, the ratio of component (A) and carrier used in terms of weight ratio is preferably 1:5 to 1:10000, and more preferably 1:10 to 1:500.

If the ratio of component (B) (component (B-1) or component (B-2)) and carrier used, or the ratio of component (A) and carrier used, deviates from the above ranges, activity may decrease. The mean particle size of the polymerization catalyst of the present invention prepared in the above manner is normally 2-200  $\mu\text{m}$ , preferably 10-150  $\mu\text{m}$ , and particularly preferably 20-100  $\mu\text{m}$ , specific surface area is normally 20-1000  $\text{m}^2/\text{g}$  and preferably 50-500  $\text{m}^2/\text{g}$ . If the mean particle size is smaller than 2  $\mu\text{m}$ , the amount of fine particles in the polymer may increase, and if the mean particle size exceeds 200  $\mu\text{m}$ , the amount of coarse particles in the polymer increases. If the specific surface area is less than 20  $\text{m}^2/\text{g}$ , polymerization may decrease, and if the specific surface area exceeds 1000  $\text{m}^2/\text{g}$ , the bulk density of the polymer may decrease. In addition, in the catalyst of the present invention, the amount of transition metal per 100 g of carrier is normally 0.05-10 g, and particularly preferably 0.1-2 g. If the amount of transition metal deviates from the above range, activity may decrease.

The supporting onto a carrier in this manner makes it possible to obtain a polymer having industrially advantageous properties including high bulk density and excellent particle size distribution.

The propylene polymer used in the present invention can be produced using the above polymerization catalyst by homopolymerization of propylene or by copolymerization of propylene and ethylene and/or  $\alpha$ -olefin having 4-20 carbons.

In this case, there are no particular restrictions on the polymerization method, and although methods such as slurry polymerization, vapor phase polymerization, block polymerization, solution polymerization or suspension polymerization may be used, slurry polymerization and vapor phase polymerization are particularly preferable.

With respect to polymerization conditions, the polymerization temperature is normally -100 to 250°C, preferably -50 to 200°C, and more preferably 0 to 130°C. In addition, the ratio of catalyst used relative to the



In preliminary polymerization, conditions should be regulated so that the intrinsic viscosity ( $\eta$ ) of the preliminary polymerization product (as measured in decalin at 135°) is 0.2 deciliters/g or more, and particularly 0.5 deciliters/g or more, and the amount of preliminary polymerization product per 1 millimole of transition metal component of the catalyst is 1-10000 g, and particularly 10-1000 g.

### [3] Propylene resin composition

The propylene resin composition of the present invention is a resin composition comprising the addition of nucleating agent to the above propylene polymer [1], the above propylene homopolymer [a] or the above propylene copolymer [a']. In general, crystallization of propylene polymer is comprised of two processes consisting of a crystal nucleation process and a crystal growth process. In the crystal nucleation process, the temperature difference with the crystallization temperature and the state of the orientation of the molecular chain and so forth are said to have an effect on the crystal nucleation rate. In particular, crystal nucleation rate is known to increase considerably if a substance is present that has the effect of promoting molecular chain orientation by means of adsorption of the molecular chain and so forth. The nucleating agent in the present invention should be that which has the effect of increasing the rate at which the crystal nucleation proceeds. Examples of substances having the effect of improving the rate at which the crystal nucleation proceeds include substances that have the effect of promoting molecular chain orientation by means of an adsorption process of the molecular chain by the polymer.

Specific examples of nucleating agents used in the present invention include high-melting temperature polymers, organic carboxylic acids or their metal salts, aromatic sulfonates or their metal salts, organic phosphate compounds or their metal salts, dibenzylidene sorbitol or its derivatives, rosin acid partial metal salts, inorganic fine particles, and imides, amides, quinacridones, quinones or their mixtures.

Examples of high-melting temperature include polyolefins such as polyethylene and polypropylene, polyvinylcycloalkanes such as polyvinylcyclohexane and polyvinylcyclopentane, syndiotactic polystyrenes,

poly 3-methylpentene-1, poly 3-methylbutene-1 and polyalkenylsilanes.

Examples of metal salts include aluminum benzoate, aluminum p-t-butylbenzoate, sodium adipate, sodium thiophene carboxylate and sodium pyrrole carboxylate.

Examples of dibenzylidene sorbitol and its derivatives include dibenzylidene sorbitol, 1,3:2,4-bis(o-3,4-dimethylbenzylidene)sorbitol, 1,3:2,4-bis(o-2,4-dimethylbenzylidene)sorbitol, 1,3:2,4-bis(o-4-ethylbenzylidene)sorbitol, 1,3:2,4-bis(o-4-chlorobenzylidene)sorbitol and 1,3:2,4-dibenzylidene sorbitol. In addition, specific examples include GELOL MD and GELOL MD-R (trade names) manufactured by Shin-Nippon Rika Co., Ltd..

Examples of rosin acid partial metal salts include PINECRYSTAL KM1600, PINECRYSTAL KM1500 and PINECRYSTAL KM1300 (trade names) available from Arakawa Chemical Industries Co., Ltd.

Examples of inorganic fine particles include talc, clay, mica, asbestos, glass fibers, glass flakes, glass beads, calcium silicate, montmorillonite, bentonite, graphite, aluminum powder, alumina, silica, diatomaceous earth, titanium oxide, magnesium oxide, tephra powder, tephra balloon, aluminum hydroxide, magnesium hydroxide, basic magnesium carbonate, dolomite, calcium sulfate, potassium titanate, barium sulfate, calcium sulfite and molybdenum sulfide.

Examples of amide compounds include adipodianilide and suberodianilide.

These nucleating agents may be used alone or in combination of any two or more thereof.

As the suitable nucleating agent for the propylene resin composition of the present invention, an organophosphoric acid metal salt represented by the general formula:











identified as a result of being concealed by noise and so forth, the respective insertion contents of (m-2,1), (r-2,1) or (1,3) were regarded as being 0.

The  $^{13}\text{C}$ -NMR spectra measurement was performed using the following apparatus and conditions.

Apparatus:  $^{13}\text{C}$ -NMR spectrometer "JNM-EX400 Model" available from Nippon Denshi Co., Ltd.;

Method: Proton complete decoupling method;

Sample concentration: 220 mg/ml;

Solvent: mixed solvent of 1,2,4-trichlorobenzene and heavy benzene (volume ratio: 90:10);

Measuring temperature: 130°C;

Pulse width: 45°;

Pulse repetition period: 4 seconds; and

Cumulative frequency: 10,000 times.

### (3) Comonomer unit content in copolymer (mol%)

The  $^{13}\text{C}$ -NMR spectra were measured under the following conditions using  $^{13}\text{C}$ -NMR spectrometer "JNM-EX400 Model" available from Nippon Denshi Co., Ltd., and then the comonomer unit contents were calculated using the method described below.

Sample concentration: 220 mg/3 ml of NMR solvent

NMR solvent: 1,2,4-trichlorobenzene/benzene- $\text{d}_6$  (90/10 vol%)

Measuring temperature: 130°C

Pulse width: 45°

Pulse repetition period: 10 seconds

Cumulative frequency: 4,000 times

#### (a) Ethylene unit

The chemical shifts and attributions of respective signals of NMR spectra as measured by  $^{13}\text{C}$ -NMR for random copolymers of propylene and ethylene are shown in Table 1.

Table 1: Signal Attributions in  $^{13}\text{C}$ -NMR Spectra of Ethylene-Propylene Copolymers

No.	Chemical Shift	Attributions
(1)	45.1-47.3	PPP $S_{\alpha\alpha}$
(2)	42.3	PPP $S_{\alpha\alpha}$
(3)	38.6	PPP $T_{\alpha\gamma}$
(4)	38.0	$S_{\alpha\gamma}$
(5)	37.5	$S_{\alpha\delta}$
(6)	36.0	PPP $S_{\alpha\beta}$
(7)	36.0	PPP $T_{\alpha\beta}$
(8)	34.9	EPP PEP $S_{\alpha\beta}$
(9)	34.6	EPP PEP $S_{\alpha\beta}$
(10)	34.1	EPP $T_{\gamma\gamma}$
(11)	33.7	EEPP $T_{\gamma\delta}$
(12)	33.3	EPE $T_{\delta\delta}$
(13)	31.6	PPP $T_{\beta\gamma}$
(14)	31.4	EPP $T_{\beta\gamma}$
(15)	31.0	PPE $T_{\beta\delta}$
(16)	30.7	PPP $S_{\alpha\beta}$
(17)	30.5	PEEE $S_{\gamma\delta}$
(18)	30.0	EEE $S_{\delta\delta}$
(19)	29.0	PPP $T_{\beta\beta}$
(20)	27.3	PEE $S_{\beta\delta}$
(21)	24.6	PEP $S_{\alpha\beta}$
(22)	21.3-22.7	P $\beta\beta$
(23)	20.6-21.3	P $\beta\beta$
(24)	19.8-20.6	P $\beta\beta$
(25)	17.6	P $\alpha\beta$
(26)	17.2	P $\alpha\gamma$

Note: E represents an ethylene unit, and chemical shifts are in ppm units.

The content of ethylene unit in the copolymer ( $\alpha$ (mol%)) was determined from the spectra measured by  $^{13}\text{C}$ -NMR according to the following equation (1):

$$\alpha = E/S \times 100 \quad (1)$$

wherein S and E respectively represent:

$$S = I_{EPE} + I_{PPE} + I_{EEE} + I_{PPP} + I_{PEE} + I_{PEP}; \text{ and}$$

$$E = I_{EEE} + 2/3(I_{PEE} + I_{EPE}) + 1/3(I_{PPE} + I_{PEP})$$

wherein

$$I_{EPE} = I(12);$$

$$I_{PPE} = I(15) + I(11) + (I(14) \cdot I(11))/2 + I(10);$$

$$I_{EEE} = I(18)/2 + I(17)/4;$$

$$I_{PPP} = I(19) + (I(6) + I(7))/2 + I(3) + I(13) + I(11) + (I(14) - I(11))/2;$$

$$I_{PEE} = I(20); \text{ and}$$

$$I_{PEP} = (I(8) + I(9) - 2 \times I(11))/4 + I(21).$$

In addition, the isotactic triad fraction of the PPP chain as a stereoregularity index (P(mol%)) of the copolymer was calculated from the following equation (2):

$$P = I_m/I \times 100 \quad (2)$$

wherein  $I_m$  and  $I$  respectively represent:

$$I_m = I(22); \text{ and}$$

$$I = I(22) + I(23) + I(24) - \{I(8) + I(9)\}/2 + I(10) + 3/2 \times I(11) + I(12) + I(13) + I(15)\}$$

wherein  $I(1)$ ,  $I(2)$  and so forth are the respective intensities of signals (1), (2) and so forth.

#### (4) Measurement of molecular weight distribution (Mw/Mn)

The molecular weight distribution (Mw/Mn) was measured by the method described in the present specification. That is, the value of Mw/Mn was calculated from values of weight-average molecular weight Mw and number-average molecular weight Mn in terms of polystyrene which were measured by GPC using the following apparatus and conditions:

GPC: Column: TOSO GMHHR-H(S)HT; and

Detector: RI Detector "WATERS 150C" for liquid chromatogram,

Measuring conditions:

Solvent: 1,2,4-trichlorobenzene;

Measuring temperature: 145°C;

Flow rate: 1.0 ml/min.;

Sample concentration: 2.2 mg/ml;

Sample amount: 160 µl;

Calibration curve: Universal Calibration; and

Analytic program: HT-GPC (Ver. 10).

#### (5) DSC measurement

The measurement was performed by the method described in the present specification using a differential scanning calorimeter ("DSC-7"

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### (5) Temperature-programmed chromatography

### (a) Measuring method

### (b) Apparatus

Flow cell: KBr cell with an optical path length of 1 mm, available from GL Science Co., Ltd.;

Valve oven: Oven "MODEL 554 (high-temperature type)" available from GL Science Co., Ltd.;

TREF oven: available from GL Science Co., Ltd.;

Two-line temperature controller: Temperature controller

"REX-C100" available from Rigaku Kogyo Co., Ltd.;

Detector: IR Detector "MIRAN 1A CVF" for liquid chromatogram,  
available from FOXBORO Co., Ltd.;

10-way valve: Electric valve available from Balco Co., Ltd.; and

Loop: 500  $\mu$ l loop available from Balco Co., Ltd.

(c) Measuring conditions

Solvent: o-dichlorobenzene;

Sample concentration: 7.5 g/l;

Sample amount: 500  $\mu$ l;

Pump discharge: 2.0 ml/min.;

Detection wave number: 3.41  $\mu$ m;

Column filler: CHROMOSORB P (30-60 mesh); and

Column temperature distribution: within  $\pm 0.2^\circ\text{C}$ .

(7) Tensile modulus

A test piece was prepared by press-forming propylene polymer, and subjected to tensile test according to JIS K-7113.

Test piece (No. 2 dumbbell): thickness: 1 mm

Cross head speed: 50 mm/min

Load cell: 100 kg

(8) Internal haze

A test piece was prepared by press-forming propylene polymer, and tested according to JIS K-7105 to measure a haze thereof. The smaller the haze value, the more excellent the transparency.

Test piece: 15 cm x 15 cm x 1 mm (thickness: 1 mm)

(9) Elastic recovery ratio

Measurement was performed in the same manner as described in Japanese Patent Application Laid-open No. 5-132590. Namely, a JIS No. 2 dumbbell as a test piece was prepared by press-forming propylene polymer. Marks were made at 25 mm intervals in the portion of the dumbbell having a constant width, and designated as  $L_0$ . After stretching the test piece at the pulling speed of 50 mm/min over a distance between chucks of from 80

mm to 160 mm using a tensile tester, the distance between the chucks was returned to the initial distance at the rate of -50 mm/min, and the distance between the marks made in the dumbbell were measured after 1 minute and designated as  $L_1$ . The elastic recovery ratio was then calculated from the following equation. A value of zero or less indicates “no recovery.”

$$[(2L_0 - L_1)/L_0] \times 100$$

wherein  $L_0$  is an initial distance between marks made on dumbbell; and  $L_1$  is a distance between marks made on dumbbell after stretching.

### (10) Anti-blocking properties

After preparing test pieces by press-forming propylene polymer and adhering the test pieces to each other under the following conditions, the peel strength was measured using a tensile tester.

Test piece: 15 mm x 62.5 mm x 2 mm

Adhesion conditions: Adhesion temperature: 40°C,

adhesion surface area: 15 mm x 31 mm, pressing load: 0.7 kg, 3 hours

Shear peeling conditions: Cross head speed: 50 mm/min

(11) Izod impact strength

A test piece was prepared by press-forming propylene polymer, and Izod impact strength was measured according to JIS K-7110 at a test piece thickness of 3 mm and ambient temperature of -5°C.

## (12) 25°C hexane soluble content (H25)

The value of H25 was measured under the following conditions.

Sample amount: 0.1-5 g;

Sample form: powder (the sample was powdered by pulverization, if pelletized)

Solvent: hexane

Elution condition: stand at 25°C for 3 or more days; and

Calculation method: calculated from the following equation:

$$H25 = [(W_0 - W_1) / W_0] \times 100 (\%).$$

(13) Measurement of a fraction extracted with boiling diethyl ether

The measurement was performed under the following conditions, using a Soxhlet extractor.

Sample amount: 1-2 g;

Sample form: powder (pelletized sample was powdered by pulverization);

Extractant: diethyl ether;

Extraction time: 10 hours;

Extraction frequency: 180 times or more; and

Calculation method: calculated from the following equation:

[Amount of a fraction extracted with diethyl ether (g) /weight of powder charged (g)] x 100.

EXAMPLE 1: Propylene homopolymer

(1) Preparation of catalyst: Synthesis of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-n-butyindenyl) zirconium dichloride

0.83 g of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(indene) (2.4 mmol) and 50 ml of ether were charged into a Schlenk's bottle. After cooling to -78°C and adding 3.1 ml (5.0 mmol) of n-BuLi (as 1.6 M hexane solution), the mixture was stirred for 12 hours at room temperature. Then, the mixture was distilled to remove the solvent therefrom, and the obtained solids were washed with 20 ml of hexane to obtain 1.1 g (2.3 mmol) of a lithium salt as an ether adduct. The thus obtained lithium salt was dissolved in 50 ml of THF and cooled to -78°C. 0.57 ml (5.3 mmol) of n-butyl bromide was slowly dropped in the resulting solution, followed by stirring for 12 hours at room temperature. The solution is distilled to remove the solvent therefrom. The obtained residues were extracted with 50 ml of hexane, and the solvent was distilled off to obtain 0.81 g (1.77 mmol) of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-n-butyindene) (yield: 74%).

Then, 0.81 g (1.77 mmol) of the obtained (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-n-butyindene) and 100 ml of ether were charged into a Schlenk's bottle under nitrogen flow. After cooling to -78°C and adding 2.7 ml (4.15 mmol) of n-BuLi (as 1.54 M hexane solution), the mixture was stirred for 12 hours at room temperature. The mixture was then distilled to remove the solvent therefrom. The thus obtained solids were washed with hexane to obtain 0.28 g (1.43 mmol) of a lithium salt as an ether

adduct.

The thus obtained lithium salt was dissolved in 50 ml of toluene under nitrogen flow. The resulting solution was cooled to  $-78^{\circ}\text{C}$ , and then a toluene suspension (50 ml) containing 0.33 g (1.42 mmol) of zirconium tetrachloride previously cooled to  $-78^{\circ}\text{C}$  was dropped therein. After completion of dropping, the mixture was stirred for 6 hours at room temperature. The mixture was then filtered, and the filtrate was distilled to remove the solvent therefrom. The resulting residues were recrystallized with dichloromethane, thereby obtaining 0.2 g (0.32 mmol) of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-n-butylindenyl)zirconium dichloride (yield: 22%).

The results of measurement by  $^1\text{H-NMR}$  (90 MHz,  $\text{CDCl}_3$ ) were as follows:  $\delta$  0.88, 0.99 (12H, dimethylsilylene), 0.7-1.0, 1.1-1.5 (18H, n-Bu), 7.0-7.6 (8H, benzene ring proton).

## (2) Polymerization of propylene

A 10-liter stainless steel autoclave was charged with 6 liters of heptane and 6 mmol of triisobutylaluminum (TIBA) and then with a catalyst component prepared by preliminarily contacting 5 mmol of methyl aluminoxane (available from Albemarle Co., Ltd.) with 5  $\mu\text{mol}$  of the above-obtained (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-n-butylindenyl)zirconium dichloride in toluene for 5 minutes. After introducing 0.05 MPa (gauge) of hydrogen into the autoclave, propylene gas was introduced thereinto until the total pressure reached 0.8 MPa (gauge). During polymerization, propylene was continuously supplied into the autoclave through a pressure regulator such that an interior of the autoclave was maintained at a constant pressure. After the propylene was polymerized at a temperature of  $50^{\circ}\text{C}$  for 30 minutes, the contents of the autoclave were taken out and then dried under reduced pressure to obtain propylene homopolymer. The resin properties of the resulting polymer were evaluated by the above method. The results are shown in Table 2.

## (3) Blending and kneading

The following additives were blended into the polypropylene homopolymer obtained above, and the resulting mixture was extruded and

granulated into pellets using a single-screw extruder (available from Tsukada Juki Seisakusho Co., Ltd.: TLC 35-20 Model).

(Additive Formulation)

Phenol-based anti-oxidant: IRGANOX 1010 available from Chiba Specialty Chemicals: 1000 ppm

Phosphorus-based anti-oxidant: P-EPQ: 500 ppm

Neutralizer: Calcium stearate: 500 ppm

Neutralizer: DHT-4A: 500 ppm

(4) Evaluation of physical properties

Physical properties of the obtained composition were evaluated by the above methods. The results are shown in Table 2.

EXAMPLE 1A

400 ml of toluene, 0.5 mmol of TIBA and 1 mmol of methyl aluminoxane were charged into a heat-dried 1-liter autoclave at room temperature in nitrogen atmosphere. After raising the temperature to 50°C while stirring, 1  $\mu$ mol of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-n-butylindenyl)zirconium dichloride was added to the autoclave. Then, propylene was supplied to the autoclave and polymerized for one hour while holding the inside pressure of the autoclave at 0.7 MPa (gauge). After completion of the polymerization reaction, the reaction product was charged into a methanol-hydrochloric acid solution, and after fully stirring, the mixture was filtered. The obtained solids were fully washed with methanol, and then dried to obtain 19.5 g of isotactic polypropylene. It was confirmed that the W25 of the resulting polymer was 90 wt%; the H25 was 15 wt%; the melting temperature ( $T_m$ ) was 71.5°C;  $\Delta H$  was 13.1 J/g; the value of  $3 \times (T_m - 120)$  was -145.5; the mmmm fraction was 44.5 mol%; the value of  $rrrr/(1-mmmm)$  was 0.029; the rrmr fraction was 2.6 mol%; the value of  $mm \times rr/(mr)^2$  was 1.05; the weight average molecular weight  $M_w$  was 499,000; the molecular weight distribution  $M_w/M_n$  was 1.97; the intrinsic viscosity was 3.18 dl/g; the 2,1-insertion fraction was 0 mol%; and the 1,3-insertion fraction was 0 mol%.

EXAMPLE 2: Propylene homopolymer

Propylene homopolymer was produced in the same manner as in

EXAMPLE 1 except that no hydrogen was introduced. The results are shown in Table 2.

### EXAMPLE 3

(1) Synthesis of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-methylindenyl)zirconium dichloride

4.4 g (12.8 mmol) of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(indene) and 100 ml of ether were charged into a Schlenk's bottle. After cooling to  $-78^{\circ}\text{C}$  and adding 16.1 ml (25.7 mmol) of n-BuLi (as 1.6 M hexane solution), the mixture was stirred for 12 hours at room temperature. Then, the mixture was distilled to remove the solvent therefrom. The obtained residues were washed with 20 ml of hexane to quantitatively obtain a lithium salt. The thus obtained lithium salt was dissolved in 100 ml of THF and cooled to  $-78^{\circ}\text{C}$ . 7.4 g (52.0 mmol) of methyl iodide was slowly dropped in the resulting solution, followed by stirring for 12 hours at room temperature. The solution is distilled to remove the solvent therefrom. The obtained residues were extracted with 50 ml of hexane, and the solvent was distilled off to obtain 4.5 g (12 mmol) of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-methylindene) (yield: 94%).

Then, 2.0 g (5.4 mmol) of the obtained (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-methylindene) and 100 ml of ether were charged into a Schlenk's bottle under nitrogen flow. After cooling to  $-78^{\circ}\text{C}$  and adding 13.5 ml (21.6 mmol) of n-BuLi (as 1.6 M hexane solution), the mixture was stirred for 12 hours at room temperature. The mixture was then distilled to remove the solvent therefrom. The obtained solids were washed with hexane to obtain 1.1 g (2.9 mmol) of a lithium salt. The lithium salt obtained above was dissolved in 100 ml of toluene under nitrogen flow. The resulting solution was cooled to  $-78^{\circ}\text{C}$ , and a toluene suspension (100 ml) containing 0.7 g (3.0 mmol) of zirconium tetrachloride previously cooled to  $-78^{\circ}\text{C}$  was dropped therein. After completion of dropping, the mixture was stirred for 6 hours at room temperature. The mixture was then filtered, and the precipitate was extracted with dichloromethane. The resulting product was recrystallized with dichloromethane/hexane, thereby obtaining 0.5 g (0.94 mmol) of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-

methylindenyl)zirconium dichloride (yield: 32%).

The results of measurement by  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) were as follows:  $\delta$  0.95, 1.05 (12H, dimethylsilylene), 2.50 (6H,  $\text{CH}_3$ ), 7.2-7.7 (8H, Ar-H).

(2) Homopolymerization of propylene

A 1-liter stainless steel autoclave was charged with 400 ml of heptane and 0.5 mmol of triisobutylaluminum and then with a catalyst component prepared by preliminarily contacting 0.5 mmol of methyl aluminoxane (available from Albemarle Co., Ltd.) with 0.5  $\mu\text{mol}$  of the above-obtained (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-methylindenyl)zirconium dichloride in toluene for 5 minutes. After introducing 0.03 MPa (gauge) of hydrogen into the autoclave, propylene gas was introduced thereinto until the total pressure reached 0.8 MPa (gauge). During polymerization, propylene was continuously supplied into the autoclave through a pressure regulator such that an interior of the autoclave was maintained at a constant pressure. After the propylene was polymerized at a temperature of  $70^\circ\text{C}$  for 1 hour, the contents of the autoclave were taken out, and then dried under reduced pressure to obtain propylene homopolymer. The resin properties of the resulting polymer was evaluated by the above method.

The results are shown in Table 2.

(3) Blending and kneading

The same blending and kneading procedures as in EXAMPLE 1 were repeated except for using additives formulated below.

(Additive Formulation)

Phenol-based anti-oxidant: IRGANOX 1010 available from Chiba Specialty Chemicals: 1000 ppm

Phosphorus-based anti-oxidant: IRGAPHOS 168 available from Chiba Specialty Chemicals: 1000 ppm

(4) Evaluation of physical properties

Evaluations were performed in the same manner as in EXAMPLE 1(4). The results are shown in Table 2.

EXAMPLE 4: Propylene copolymer

(1) Preparation of catalyst

(a) Production of (1,2'-ethylene)(2,1'-ethylene)bis(3-methylindene)

1.12 g (3.94 mmol) of (1,2'-ethylene)(2,1'-ethylene)bis(indene) was dissolved in 50 ml of dehydrated ether under nitrogen flow. The obtained solution was cooled to  $-78^{\circ}\text{C}$ , and then 5.01 ml of a hexane solution containing n-butyl lithium at a concentration of 1.57 mol/l (n-butyl lithium: 7.87 mmol) was dropped into the solution for 30 minutes. Then, the temperature was raised to room temperature, and the mixture was stirred for 8 hours. The mixture was distilled under reduced pressure to remove the ether solvent therefrom, and the obtained residues were washed with hexane to obtain 1.12 g (3.02 mmol) of dilithium salt as an ether adduct. The dilithium salt was then dissolved in 50 ml of dehydrated tetrahydrofuran and cooled to  $-78^{\circ}\text{C}$ . After 10 ml of a tetrahydrofuran solution containing 0.42 ml (6.74 mmol) of methyl iodide was dropped into the solution for 20 minutes, the temperature was raised to room temperature followed by stirring for 8 hours. After distilling off the solvent under reduced pressure, the residues were extracted with ethyl acetate. After washing the extract with water and drying the organic phase thereof with anhydrous magnesium sulfate, the liquid was filtered and the filtrate was dried and solidified under reduced pressure to obtain 0.87 g (2.78 mmol) of (1,2'-ethylene)(2,1'-ethylene)bis(3-methylindene) as the aimed product at a yield of 70.5%. The obtained product was in the form of a mixture of isomers being different in position of double bond in the five-membered ring from each other.

(b) Production of dilithium salt of (1,2'-ethylene)(2,1'-ethylene)-bis(3-methylindene)

0.87 g (2.78 mmol) of (1,2'-ethylene)(2,1'-ethylene)bis(3-methylindene) was dissolved in 35 mmol of ether under nitrogen flow and cooled to  $-78^{\circ}\text{C}$ . After 3.7 ml of a hexane solution containing n-butyl lithium at a concentration of 1.57 mol/l (n-butyl lithium: 5.81 mmol) was dropped into the solution for 30 minutes, the temperature was raised to room temperature and the mixture was stirred for 8 hours. The mixture was distilled under reduced pressure to remove the solvent therefrom, and the obtained residues were washed with hexane to obtain 1.03 g (2.58 mmol) of dilithium salt as an ether adduct at a yield of 92.8%.

<sup>1</sup>H-NMR (THF-d<sub>8</sub>) (δ, ppm): 2.20 (6H, s), 3.25 (8H, s), 6.0-7.4 (8H, m)

1.03 g (2.58 mmol) of the ether adduct of (1,2'-ethylene)(2,1'-ethylene)-bis(3-methylindene) dilithium salt was suspended in 25 ml of toluene and cooled to -78°C. After adding a toluene suspension (20 ml) containing 0.60 g (2.58 mmol) of zirconium tetrachloride to the above suspension for 20 minutes, the temperature was raised to room temperature and the mixture was stirred for 8 hours, followed by filtering off the toluene supernatant therefrom. The obtained residues were then extracted twice with 50 ml of dichloromethane. After distilling off the solvent under reduced pressure, the residues were recrystallized with dichloromethane/hexane to obtain 0.21 g of (1,2'-ethylene)(2,1'-ethylene)bis(3-methylindenyl) zirconium dichloride at a yield of 17.3%.

The results of <sup>1</sup>H-NMR measurement were as follows:

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): 2.48 (6H, s), 3.33-3.85 (8H, m), 6.9-7.6 (8H, m)

## (2) Copolymerization of propylene and ethylene

1.2 liters of toluene, 1.5 mmol of triisobutylaluminum, 10 mmol (in terms of aluminum) of methyl aluminoxane (available from Albemarle Co., Ltd.) and 20  $\mu$ mol of (1,2'-ethylene)(2,1'-ethylene)bis(3-methylindenyl) zirconium dichloride were charged into a 2-liter stainless steel autoclave. The resulting mixture was heated to 30°C, and a mixed gas of ethylene and propylene (molar ratio of ethylene to propylene = 1:100) was introduced thereinto. Surplus gas was discharged so as to control the total pressure in the autoclave to 0.7 MPa (gauge). After propylene and ethylene were polymerized for 60 minutes while maintaining a uniform gas composition ratio in the system, the contents were removed from the autoclave, followed by drying under reduced pressure, thereby obtaining a propylene copolymer. Procedures for blending and kneading as well as evaluation of resin properties and physical properties were performed in the same manner as in EXAMPLE 1. The results are shown in Table 2.

COMPARATIVE EXAMPLE 1: Propylene homopolymer

#### (1) Preparation of magnesium compound

After a glass reactor equipped with a stirrer having a capacity of about 6 liters was fully purged with nitrogen, about 2,430 g of ethanol, 16 g of iodine and 160 g of magnesium metal were charged into the reactor. The contents of the reactor were heated while stirring and reacted with each other under reflux until hydrogen gas was no longer generated from the reaction system to obtain a solid reaction product. The reaction solution containing the solid reaction product was dried under reduced pressure to obtain a magnesium compound.

#### (2) Preparation of solid catalyst component (A)

160 g of the magnesium compound (uncrushed) obtained in the above step (1), 80 ml of purified heptane, 24 ml of silicon tetrachloride and 23 ml of diethyl phthalate were charged into a 5-liter glass reactor fully purged with nitrogen gas. 770 ml of titanium tetrachloride was added to the mixture while holding the temperature inside the system at 80°C and stirring, and the contents of the reactor were reacted with each other at 110°C for 2 hours. Then, the solid component was separated from the reaction mixture, and washed with purified heptane at 90°C. Moreover, the obtained solid component was mixed with 1,220 ml of titanium tetrachloride, and the mixture was reacted at 110°C for 2 hours. The resulting reaction product was sufficiently washed with purified heptane to obtain a solid catalyst component (A).

#### (3) Vapor phase polymerization of propylene

The solid catalyst component obtained in the above step (2) at a feed rate of 6.0 g/hr, triisobutyl aluminum (TIBA) at 0.2 mol/hr, 1-allyl-3,4-dimethoxybenzene (ADMB) at 0.012 mol/hr, cyclohexylmethyl dimethoxysilane (CHMDMS) at 0.012 mol/hr and propylene at 37 kg/hr were supplied to a 200-liter polymerization vessel, and polymerized at 70°C under 2.8 MPa (gauge).

#### (4) Blending and kneading

2,5-dimethyl-2,5-di-(t-butylperoxy)-hexane was mixed with the resulting polypropylene powder followed by blending with the same additives as used in EXAMPLE 1. The resulting composition was extruded

[illegible]

### (5) Evaluation of resin properties and physical properties

Evaluation was performed in the same manner as in EXAMPLE 1.

The results are shown in Table 2.

### REFERENCE EXAMPLE: Affinity PL1880

Physical properties of pellets "Affinity PL1880" (tradename) available from Dow Chemical Japan, Co., Ltd., were evaluated in the same manner as in EXAMPLE 1(4). The results are shown in Table 2.

### COMPARATIVE EXAMPLE 2: Propylene homopolymer

A 1-liter stainless steel autoclave was charged with 400 ml of heptane, 0.5 mmol of triisobutyl aluminum, and a catalyst component prepared by preliminarily contacting 2  $\mu$ mol of dimethylanilinium (pentafluorophenyl)borate with 1  $\mu$ mol of (tertiary butylamide) dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silane titanium dichloride produced by the same method as in Example 1 of Japanese Patent Application Laid-open No. 3-163088, for 5 minutes in toluene. After introducing 0.03 MPa (gauge) of hydrogen into the autoclave, propylene gas was introduced thereinto until the total pressure reached 0.8 MPa (gauge). During polymerization, propylene was continuously supplied through a pressure regulator such that an interior of the autoclave was maintained at a constant pressure. After the propylene was polymerized for 1 hour at a temperature of 70°C, the contents of the autoclave were taken out, and then dried under reduced pressure to obtain a propylene homopolymer. Procedures for blending and kneading as well as evaluation of resin properties and physical properties were performed in the same manner as in EXAMPLE 1. The results are shown in Table 2.

### EXAMPLE 5: Addition of nucleating agent

The same procedure as in EXAMPLE 1 was repeated except that the additives formulated below were added to the propylene homopolymer obtained in EXAMPLE 1. The results are shown in Table 3.

(Additive Formulation)

Phenol-based anti-oxidant: IRGANOX 1010 available from Chiba Specialty Chemicals: 1000 ppm



Polypropylene E105GM (available from Idemitsu Petrochemicals, Co., Ltd.), and the resulting blended mixture was extruded and granulated into pellets using a single-screw extruder ("TLC35-20 Model" available from Tsukada Juki Seisakusho Co., Ltd.). Procedures for evaluation of physical properties were performed in the same manner as in EXAMPLE 1(4). The results are shown in Table 4.

#### EXAMPLE 11: Effect of addition of modifier

The same procedure as in EXAMPLE 10 was repeated except that the pellets obtained in EXAMPLE 1 were blended in an amount of 60 wt%. The results are shown in Table 4.

#### EXAMPLE 12: Effect of addition of modifier

The same procedure as in EXAMPLE 10 was repeated except that the pellets obtained in EXAMPLE 1 were blended in an amount of 30 wt%. The results are shown in Table 4.

#### COMPARATIVE EXAMPLE 3

Physical properties of Polypropylene "E105GM" (available from Idemitsu Petrochemicals, Co., Ltd.) were evaluated by the same method as in EXAMPLE 1(4). The results are shown in Table 4.

#### COMPARATIVE EXAMPLE 4

The same procedure as in EXAMPLE 10 was repeated except that the polymer obtained in COMPARATIVE EXAMPLE 2 was blended in an amount of 50 wt% into Polypropylene "E105GM" (available from Idemitsu Petrochemicals, Co., Ltd.). The results are shown in Table 4.

#### EXAMPLE 13: Propylene homopolymer

A 1-liter stainless steel pressure autoclave equipped with a stirrer was heated to 80°C, fully dried under reduced pressure, returned to atmospheric pressure by introducing dry nitrogen thereinto, and then cooled to room temperature. 400 ml of dry deoxygenated heptane and 0.5 ml of a 2.0 M heptane solution of triisobutyl aluminum (1.0 mmol) were charged into the autoclave under dry nitrogen flow, followed by stirring at 350 rpm for a while. Then, a 50 ml Schlenk's tube fully purged with nitrogen was charged with 10 ml of cyclohexane and 0.5 ml of a 2 M heptane solution of triisobutyl aluminum (1.0 mmol) and then with 1.0 ml of a 4 M cyclohexane

solution of dimethylanilinium tetrakis(pentafluorophenyl)borate (4.0 mmol) and 4  $\mu\text{mol}$  of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(3-n-butyindenyl) zirconium dichloride obtained in EXAMPLE 1, followed by stirring for 60 minutes at room temperature. The resulting catalyst slurry was quickly charged into the autoclave. Then, hydrogen was introduced into the autoclave until reaching 0.03 MPa (gauge). Subsequently, the contents of the autoclave were stirred at 400 rpm, and propylene was slowly introduced until the total pressure thereof reached 0.8 MPa (gauge) while simultaneously slowly raising the temperature to 50°C. The propylene was polymerized for 30 minutes.

After completion of the polymerization reaction, unreacted propylene was removed by depressurization. The reaction mixture was charged into 2 liters of methanol to precipitate polypropylene. Then, the reaction mixture was filtered, and the resulting residue was dried to obtain polypropylene. The obtained polypropylene was evaluated by the same method as in EXAMPLE 1. The results are shown in Table 5.

#### EXAMPLE 14: Propylene homopolymer

A 1 liter stainless steel pressure autoclave equipped with a stirrer was heated to 80°C, fully dried under reduced pressure, returned to atmospheric pressure by introducing dry nitrogen thereinto, and then cooled to room temperature. 400 ml of dry deoxygenated heptane, 1.0 ml of a 2.0 M heptane solution of triisobutyl aluminum (2.0 mmol) and 0.8 ml of a heptane slurry (2.0  $\mu\text{mol}/\text{ml}$ ) of dimethylanilinium tetrakis (pentafluorophenyl) borate (1.6  $\mu\text{mol}$ ) were charged into the autoclave under dry nitrogen flow, followed by stirring for 5 minutes at room temperature at 350 rpm. Subsequently, the resulting mixture was mixed with 4  $\mu\text{mol}$  of the above-obtained (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(3-n-butyindenyl)zirconium dichloride, and then hydrogen was introduced into the autoclave until reaching 0.03 MPa (gauge). Then, the contents of the autoclave were stirred at 400 rpm, and propylene was slowly introduced until the total pressure thereof reached 0.8 MPa (gauge) while simultaneously slowly raising the temperature to 50°C. The propylene was polymerized for 30 minutes. After completion of the polymerization

[illegible]

### EXAMPLE 15

(1) Synthesis of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-trimethylsilylmethylindenyl)zirconium dichloride

3.0 g (6.97 mmol) of a lithium salt of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(indene) was dissolved in 50 ml of THF in a Schlenk's bottle and cooled to -78°C. 2.1 ml (14.2 mmol) of iodomethyltrimethylsilane was slowly dropped in the solution and stirred for 12 hours at room temperature. The resulting mixture was distilled to remove the solvent therefrom, and the obtained residues were mixed with 50 ml of ether and washed with saturated ammonium chloride solution. After separating the liquid from the mixture, the organic phase was dried to remove the solvent therefrom to obtain 3.04 g (5.88 mmol) of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-trimethylsilylmethylinden e) (yield: 84%).

Next, 3.04 g (5.88 mmol) of the thus obtained (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-trimethylsilylmethylindene) and 50 ml of ether were charged into a Schlenk's bottle under nitrogen flow. After cooling to -78°C and adding 7.6 ml (11.7 mmol) of n-BuLi (as 1.54 M hexane solution), the mixture was stirred for 12 hours at room temperature. Then, the mixture was distilled to remove the solvent therefrom, and the obtained solids were washed with 40 ml of hexane to obtain 3.06 g (5.07 mmol) of a lithium salt as an ether adduct (yield: 73%).

The results of measurement by  $^1\text{H}$ -NMR (90 MHz,  $\text{THF-d}_8$ ) were as follows:  $\delta$  0.04 (s, 18H, trimethylsilyl), 0.48 (s, 12H, dimethylsilylene), 1.10 (t, 6H, methyl), 2.59 (s, 4H, methylene), 3.38 (q, 4H, methylene), 6.2-7.7 (m, 8H, Ar-H).

The thus obtained lithium salt was dissolved in 50 ml of toluene under

nitrogen flow. The solution was cooled to  $-78^{\circ}\text{C}$ , and a toluene suspension (20 ml) containing 1.2 g (5.1 mmol) of zirconium tetrachloride preliminarily cooled to  $-78^{\circ}\text{C}$  was dropped into the solution. After completion of dropping, the mixture was stirred for 6 hours at room temperature. The reaction solution was then distilled to remove the solvent therefrom. The resulting residues were recrystallized with dichloromethane to obtain 0.9 g (1.33 mmol) of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(3-trimethylsilylmethylindenyl)zirconium dichloride (yield: 26%).

The results of measurement by  $^1\text{H-NMR}$  (90 MHz,  $\text{CDCl}_3$ ) were as follows:  $\delta$  0.0 (s, 18H, trimethylsilyl), 1.02, 1.12 (s, 12H, dimethylsilylene), 2.51 (dd, 4H, methylene), 7.1-7.6 (m, 8H, Ar-H).

## (2) Homopolymerization

The same polymerization procedure as in EXAMPLE 1 (2) was repeated except for using (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(3-trimethylsilylmethylindenyl)zirconium dichloride instead of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-n-butylindenyl)zirconium dichloride. The obtained polymer was evaluated by the same method as in EXAMPLE 1. The results are shown in Table 5.

## EXAMPLE 15A

400 ml of toluene, 0.5 mmol of TIBA and 0.5 mmol of methyl aluminoxane were charged into a heat-dried 1-liter autoclave at room temperature under nitrogen flow. After raising the temperature to  $50^{\circ}\text{C}$  while stirring, 0.5  $\mu\text{mol}$  of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(3-trimethylsilylmethylindenyl)zirconium dichloride was added to the autoclave. Then, propylene was supplied to the autoclave and polymerized for one hour while holding the inside pressure of the autoclave at 0.7 MPa (gauge). After completion of the polymerization reaction, the reaction product was charged into a methanol-hydrochloric acid solution and after fully stirring, the mixture was filtered. The obtained solids were fully washed with methanol and then dried to obtain 70.1 g of isotactic polypropylene. It was confirmed that the W25 value of the resulting polymer was 92 wt%, the H25 value was 16 wt%, the melting temperature ( $T_m$ ) was  $73.5^{\circ}\text{C}$ ,  $\Delta H$  was 5.2 J/g, the value of  $3 \times (T_m - 120)$  was  $-139.5$ , the

mmmm fraction was 39.8 mol%, the value of rrrr/(1-mmmm) was 0.032, the rrmr fraction was 2.6 mol%, the value of mm x rr/(mr)<sup>2</sup> was 1.33, the weight average molecular weight Mw was 664,000, the molecular weight distribution Mw/Mn was 2.46, the intrinsic viscosity was 3.39 dl/g, the 2,1-insertion fraction was 0 mol%, and the 1,3-insertion fraction was 0 mol%.

#### EXAMPLE 16

##### (1) Synthesis of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-ethoxymethylindenyl)zirconium dichloride

4.1 g (9.50 mmol) of a lithium salt of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(indene) was dissolved in 50 ml of THF in a Schlenk's bottle and cooled to -78°C. 1.9 ml (20.5 mmol) of chloromethyl ethyl ether were slowly dropped into the solution and stirred for 12 hours at room temperature. The resulting mixture was distilled to remove the solvent therefrom, and the obtained residues were mixed with 50 ml of ether and hydrolyzed with saturated ammonium chloride solution. After separating the liquid from the mixture, the organic phase was dried to remove the solvent therefrom to obtain 3.43 g (7.40 mmol) of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-ethoxymethylindene) (yield: 78%).

Next, 3.43 g (7.40 mmol) of the thus obtained (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-ethoxymethylindene) and 50 ml of ether were charged into a Schlenk's bottle under nitrogen flow. After cooling to -78°C and adding 9.4 ml (14.8 mmol) of n-BuLi (as 1.57 M hexane solution), the mixture was stirred for 12 hours at room temperature. Then, the mixture was distilled to remove the solvent therefrom, and the obtained solids were washed with 50 ml of hexane to obtain 1.07 g (1.96 mmol) of a lithium salt as an ether adduct (yield: 26%). The thus obtained lithium salt was then dissolved in 50 ml of toluene under nitrogen flow. The solution was cooled to -78°C, and a toluene suspension (20 ml) of 0.46 g (1.96 mmol) of zirconium tetrachloride preliminarily cooled to -78°C was dropped into the solution. After completion of dropping, the mixture was stirred for 6 hours at room temperature. The reaction solution was then distilled to remove the solvent therefrom. The resulting residues were

extracted with 40 ml of hexane to obtain 0.24 g (0.39 mmol) of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-ethoxymethylindenyl)zirconium dichloride (yield: 20%).

## (2) Homopolymerization

The same polymerization procedure as in EXAMPLE 1 (2) was repeated except for using (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(3-ethoxymethylindenyl)zirconium dichloride instead of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-n-butylindenyl)zirconium dichloride. The obtained polymer was evaluated by the same method as in EXAMPLE 1. The results are shown in Table 5.

## EXAMPLE 16A

The same procedure as in EXAMPLE 1A was repeated except for using (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-ethoxymethylindenyl)zirconium dichloride instead of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)bis(3-n-butylindenyl)zirconium dichloride, to obtain 36.4 g of isotactic polypropylene. It was confirmed that the W25 value of the resulting polymer was 91 wt%, the H25 value was 16 wt%, the melting temperature ( $T_m$ ) was 72.2°C,  $\Delta H$  was 3 J/g, the value of  $3 \times (T_m - 120)$  was -143.4, the mmmm fraction was 41.9 mol%, the value of  $rrrr/(1-mmmm)$  was 0.040, the rmmr fraction was 3.7 mol%, the value of  $mm \times rr/(mr)^2$  was 1.24, the weight average molecular weight  $M_w$  was 595,000, the molecular weight distribution  $M_w/M_n$  was 4.87, the intrinsic viscosity was 3.33 dl/g, the 2,1-insertion fraction was 0 mol%, and the 1,3-insertion fraction was 0 mol%.

## COMPARATIVE EXAMPLE 5

### (1) Synthesis of complex

Bis(2-phenylindenyl)zirconium dichloride was synthesized according to the method described in "Science", 267, 217 (1995).

### (2) Homopolymerization

A 1-liter stainless steel pressure autoclave equipped with a stirrer was heated to 80°C, fully dried under reduced pressure, returned to atmospheric pressure by introducing dry nitrogen thereinto, and then cooled to room temperature. 400 ml of dry deoxygenated heptane and 1.0 ml of a 2.0 M

heptane solution of triisobutyl aluminum (2.0 mmol) were charged into the autoclave under dry nitrogen flow, followed by stirring at 350 rpm for a while. A toluene slurry of methyl aluminoxane (2.04 mmol/ml, 4.0 ml, 8 mmol) and a heptane slurry of the above-obtained bis(2-phenylindenyl)zirconium dichloride (10  $\mu$ mol/ml, 0.8 ml, 8.0  $\mu$ mol) were added to the autoclave. Subsequently, the contents of the autoclave were stirred at 400 rpm, and propylene was slowly introduced until the total pressure thereof reached 0.8 MPa (gauge) while simultaneously slowly raising the temperature to 30°C. The propylene was polymerized for 60 minutes. After completion of the polymerization reaction, unreacted propylene was removed by depressurization. The reaction solution was charged into a vat, air-dried overnight and then dried under reduced pressure at 60°C to obtain polypropylene. The resulting polypropylene was evaluated by the same method as in EXAMPLE 1. The results are shown in Table 5.

#### COMPARATIVE EXAMPLE 6

##### (1) Synthesis of complex

[1-(9-fluorenyl)-2-(1-(5,6-cyclopenta-2-methyl-1-indenyl)ethane)] zirconium dichloride was synthesized according to the method described in WO 99/52950.

##### (2) Homopolymerization

A 1-liter stainless steel pressure autoclave equipped with a stirrer was heated to 80°C, fully dried under reduced pressure, returned to atmospheric pressure by introducing dry nitrogen thereinto, and then cooled to room temperature. 400 ml of dry deoxygenated toluene and 1.0 ml of a 2.0 M heptane solution of triisobutyl aluminum (2.0 mmol) were charged into the autoclave under dry nitrogen flow, followed by stirring at 350 rpm for a while. A toluene slurry of methyl aluminoxane (2.04 mmol/ml, 4.0 ml, 8 mmol) and a heptane slurry of the above-obtained rac-[1-(9-fluorenyl)-2-(1-(5,6-cyclopenta-2-methyl-1-indenyl)ethane)] zirconium dichloride (10  $\mu$ mol/ml, 0.8 ml, 8.0  $\mu$ mol) were added to the autoclave. Subsequently, the contents of the autoclave were stirred at 400 rpm, and the propylene was slowly introduced until the total pressure

thereof reached 0.8 MPa (gauge) while simultaneously slowly raising the temperature to 30°C. The propylene was polymerized for 60 minutes. After completion of the polymerization reaction, unreacted propylene was removed by depressurization. The reaction solution was charged into a vat, air-dried overnight and then dried under reduced pressure at 60°C to obtain polypropylene. The resulting polypropylene was evaluated by the same method as in EXAMPLE 1. The results are shown in Table 5.

Table 2-1

Item	Ex. 1	Ex. 2	Ex. 3	Ex. 4
Comonomer content mol%	--	--	--	10
W25 wt%	93	90	80	56
H25 wt%	17	15	15	42
Tm °C	n.d.	n.d.	70	76
ΔH J/g	n.d.	n.d.	7	19
3 x (Tm-120)	n.d.	n.d.	-150	-132
mmmm fraction mol%	41	41	46	--
P mol%	--	--	--	76
rrrr/(l-mmmm)	0.04	0.04	0.04	--
rmrm fraction mol%	3.2	3.2	2.6	--
mm x rr/(mr) <sup>2</sup>	1.2	1.2	1.3	--
Mw/Mn	2.4	2.0	2.5	6.1
[η] dl/g	2.5	4.4	4.4	0.7
2,1-insertion fraction mol%	0	0	0	--
1,3-insertion fraction mol%	0	0	0	--
Boiling diethyl ether extraction amount wt%	30	29	25	56
Tc °C	n.d.	n.d.	n.d.	18
Tensile modulus MPa	31	34	52	60
Internal haze %	4	3	4	10
Elastic recovery ratio %	69	78	33	28
Anti-blocking properties kg/cm <sup>2</sup>	5	5	4	6
Izod impact strength kJ/m <sup>2</sup>	2.8	3.4	2.5	5.0

n.d.: Not determined

Izod impact strength: With notch, measured at -5°C

Table 2-2

Item	Comp. Ex. 1	Comp. Ex. 2	Ref. Ex.
Comonomer content mol%	--	--	--
W25 wt%	30	99	--
H25 wt%	6	100	--
Tm °C	159	n.d.	--
ΔH J/g	61	n.d.	--
3 x (Tm-120)	117	n.d.	--
mmmm fraction mol%	65	2	--
P mol%	--	--	--
rrrr/(l-mmmm)	0.23	0.114	--
rmrm fraction mol%	1.4	15.3	--
mm x rr/(mr) <sup>2</sup>	6.1	0.2	--
Mw/Mn	2.7	2.2	--
[η] dl/g	2.1	1.9	--
2,1-insertion fraction mol%	0	4.4	--
1,3-insertion fraction mol%	0	0	--
Boiling diethyl ether extraction amount wt%	12	63	--
Tc °C	104	n.d.	--
Tensile modulus MPa	330	2	85
Internal haze %	60	4	10
Elastic recovery ratio %	No recovery	79	No recovery
Antiblocking properties kg/cm <sup>2</sup>	0	No peeling	3
Izod impact strength kJ/m <sup>2</sup>	2.1	4.3	Not ruptured

n.d.: Not determined

Izod impact strength: With notch, measured at -5°C

Table 3-1

Item	Ex. 1	Ex. 5	Ex. 6
Nucleating agent	--	Gelall MD	Gelall MD
Amount of nucleating agent added ppm	--	1000	2000
Tm °C	n.d.	n.d.	64
Tc °C	n.d.	n.d.	n.d.
Tensile modulus MPa	30	32	35
Internal haze %	4	5	5
Elastic recovery ratio %	69	70	72
Izod impact strength kJ/m <sup>2</sup>	2.8	3.2	2.9

Izod impact strength: With notch, measured at -5°C

Table 3-2

Item	Ex. 7	Ex. 8	Ex. 9
Nucleating agent	Gelall MD	Gelall MD	NA-11
Amt. of nucleating agent added ppm	5000	10000	2000
T <sub>m</sub> °C	65	64	64
T <sub>c</sub> °C	n.d.	n.d.	n.d.
Tensile modulus MPa	41	42	32
Internal haze %	5	4	5
Elastic recovery ratio %	75	76	76
Izod impact strength kJ/m <sup>2</sup>	5.0	2.9	7.1

Izod impact strength: With notch, measured at -5°C

Table 4-1

Item	Ex. 10	Ex. 11	Ex. 12
Tensile modulus MPa	190	230	560
Internal haze %	33	43	54
Elastic recovery ratio %	20	1	No recovery
Izod impact strength kJ/m <sup>2</sup>	2.5	2.4	1.9

Izod impact strength: With notch, measured at -5°C

Table 4-2

Item	Comp. Ex. 1	Comp. Ex. 3	Comp. Ex. 4
Tensile modulus MPa	330	1500	240
Internal haze %	60	44	71
Elastic recovery ratio %	No recovery	No recovery	No recovery
Izod impact strength kJ/m <sup>2</sup>	2.1	1.9	1.6

Izod impact strength: With notch, measured in -5°C

Table 5-1

Item	Ex. 13	Ex. 14	Ex. 15	Ex. 16
Comonomer content mol%	--	--	--	--
W25 wt%	91	90	90	91
H25 wt%	14	15	16	15
T <sub>m</sub> °C	n.d.	n.d.	n.d.	n.d.
ΔH J/g	n.d.	n.d.	n.d.	n.d.
3 x (T <sub>m</sub> -120)	n.d.	n.d.	n.d.	n.d.
mmmm fraction mol%	42	42	42	44
P mol%	--	--	--	--
rrrr/(l-mmmm)	0.04	0.04	0.04	0.04
rmm fraction mol%	3.0	3.2	3.2	2.6
mm x rr/(mr) <sup>2</sup>	1.2	1.2	1.2	1.3
Mw/Mn	2.3	2.4	2.5	2.4
[η] dl/g	1.3	1.3	2.3	2.5
2,1-insertion fraction mol%	0	0	0	0
1,3-insertion fraction mol%	0	0	0	0
Boiling diethyl ether extraction amount wt%	28	27	26	28
T <sub>c</sub> °C	n.d.	n.d.	n.d.	18
Tensile modulus MPa	35	36	37	35
Internal haze %	3	4	4	3
Elastic recovery ratio %	68	67	70	69
Antiblocking properties kg/cm <sup>2</sup>	4	5	5	4
Izod impact strength kJ/m <sup>2</sup>	3.2	3.0	3.5	3.4

n.d.: Not determined

Izod impact strength: With notch, measured in -5°C

Table 5-2

Item	Comp. Ex. 5	Comp. Ex. 6
Comonomer content mol%	--	--
W25 wt%	99	98
H25 wt%	50	25
T <sub>m</sub> °C	142.0	121.2
ΔH J/g	5.5	1.1
3 x (T <sub>m</sub> -120)	66	-3.3
mmmm fraction mol%	27	36
P mol%	--	--
rrrr/(l-mmmm)	0.04	0.05
rmrm fraction mol%	9.7	1.1
mm x rr/(mr) <sup>2</sup>	0.4	1.5
M <sub>w</sub> /M <sub>n</sub>	2.8	2.5
[η] dl/g	1.22	1.44
2,1-insertion fraction mol%	0	0
1,3 insertion fraction mol%	0	0
Boiling diethyl ether extraction amount wt%	--	--
T <sub>c</sub> °C	--	--
Tensile modulus MPa	8	26
Internal haze %	20.6	15.3
Elastic recovery ratio %	88	93
Antiblocking properties kg/cm <sup>2</sup>	No peeling	5
Izod impact strength kJ/m <sup>2</sup>	2.3	2.9

Izod impact strength: With notch, measured in -5°C

### Industrial Applicability

The propylene polymer, propylene homopolymer, propylene copolymer and resin composition and molded product composed of the polymers have a less stickiness as well as excellent softness and transparency, and are suitable for use in films, sheets, containers, automobile interior trims housings of home appliances, and so forth. Examples of films include food packaging films and agricultural films, and examples of containers include transparent cases, transparent boxes and decorative boxes. In addition, they can also be used as alternatives to soft vinyl dichloride resin. The propylene resin modifier of the present invention is capable of forming molded products that are soft, and have a less stickiness and excellent compatibility with polyolefin resin.

7. The following information is provided for the year ended 31 December 2014:

- $$\Delta H \geq 3 \times (T_m - 120).$$

2. The propylene polymer according to claim 1, having a fraction (W25) eluted at a temperatures up to 25°C by temperature-programmed chromatography, of from 20-100 wt%.

- $$[\text{rrrr}/(1\text{-mmmm})] \leq 0.1$$

- $$(\text{mm}) \times (\text{rr})/(\text{mr})^2 \leq 2.0$$

5. The propylene homopolymer according to claim 3, having a molecular weight distribution (Mw/Mn) of 4 or less as measured by gel permeation chromatography (GPC) and/or an intrinsic viscosity  $[\eta]$  of from 0.5-15.0 dl/g as measured at 135°C in tetralin.

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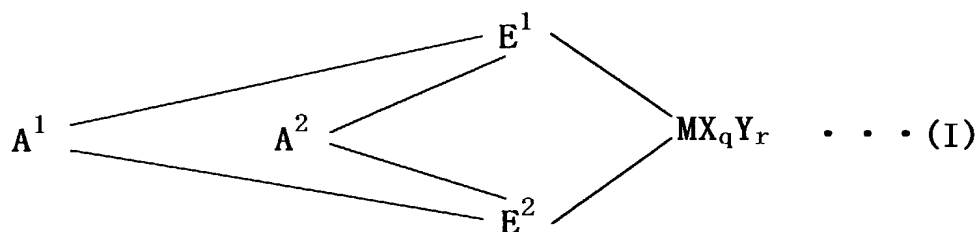
- (1) a stereoregularity index (P) of 55-90 mol% as determined by  $^{13}\text{C}$ -NMR measurement; and
- (2) a fraction (W25) eluted at a temperatures up to  $25^{\circ}\text{C}$  by temperature-programmed chromatography, of from 20-100 wt%.

7. The propylene copolymer according to claim 6 having a molecular weight distribution ( $M_w/M_n$ ) of 4 or less as measured by gel permeation chromatography (GPC) and/or an intrinsic viscosity  $[\eta]$  of from 0.5-15.0 dl/g as measured at  $135^{\circ}\text{C}$  in tetralin.

8. The propylene homopolymer according to claim 3 produced by polymerizing propylene in the presence of a polymerization catalyst containing:

(A) a transition metal compound represented by the general formula

(I):



wherein M is a metal element of Groups 3 to 10 of the Period Table or lanthanoid series;

$\text{E}^1$  and  $\text{E}^2$  are respectively a ligand selected from the group consisting of substituted cyclopentadienyl, indenyl, substituted indenyl, heterocyclopentadienyl, substituted heterocyclopentadienyl, amide, phosphide, a hydrocarbon group and a silicon-containing group, which form a cross-linked structure via  $\text{A}^1$  and  $\text{A}^2$  and may be the same or different;

X is a ligand capable of forming a  $\sigma$ -bond or  $\pi$ -bond with the proviso that when a plurality of X groups are present, these groups may be the same or different, and may be cross-linked with the other X group,  $\text{E}^1$ ,  $\text{E}^2$  or Y;

Y is a Lewis base with the proviso that when a plurality of Y groups are present, these groups may be same or different, and may be cross-linked with the other Y group,  $\text{E}^1$ ,  $\text{E}^2$  or X;



[illegible]

... (II)

11. The propylene homopolymer according to claim 9, wherein the transition metal compound represented by the general formula (II) is a transition metal compound represented by the general formula (III):



that when a plurality of X groups are present, these groups may be the same or different, and may be cross-linked with the other X group, E<sup>1</sup>, E<sup>2</sup> or Y;

Y is a Lewis base with the proviso that when a plurality of Y groups are present, these groups may be same or different, and may be cross-linked with the other Y group, E<sup>1</sup>, E<sup>2</sup> or X;

A<sup>1</sup> and A<sup>2</sup> are divalent cross-linking groups capable of bonding the two ligands E<sup>1</sup> and E<sup>2</sup> to each other, are independently a C<sub>1</sub>-C<sub>20</sub> hydrocarbon group, a C<sub>1</sub>-C<sub>20</sub> halogen-containing hydrocarbon group, a silicon-containing group, a germanium-containing group, a tin-containing group, -O-, -CO-, -S-, -SO<sub>2</sub>-, -Se-, -NR<sup>1</sup>-, -PR<sup>1</sup>-, -P(O)R<sup>1</sup>-, -BR<sup>1</sup>- or -AlR<sup>1</sup>- wherein R<sup>1</sup> is a hydrogen atom, a halogen atom, a C<sub>1</sub>-C<sub>20</sub> hydrocarbon group or a C<sub>1</sub>-C<sub>20</sub> halogen-containing hydrocarbon group, and may be the same or different;

q is an integer of 1 to 5 given by the formula:

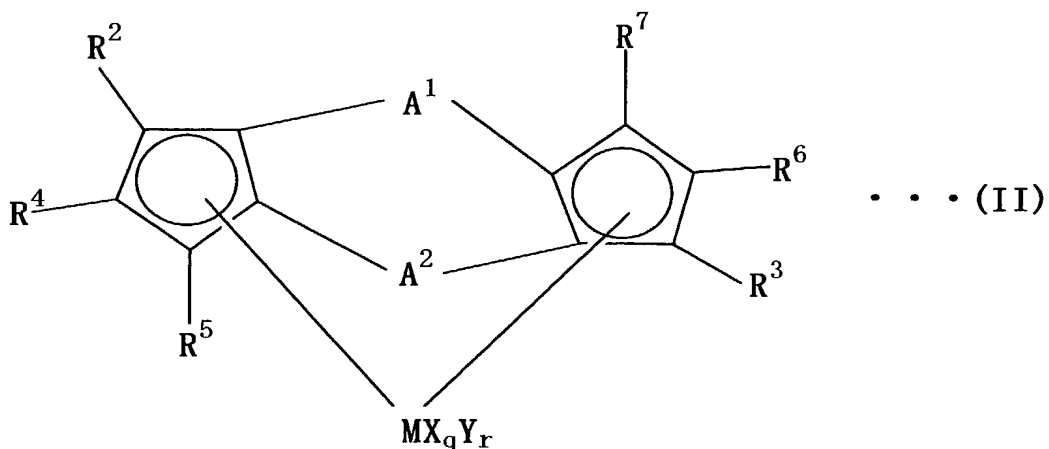
[(valence of M) - 2]; and

r is an integer of 0 to 3, and

(B) a component selected from the group consisting of (B-1) a compound capable of forming an ionic complex by reacting with the transition metal compound (A) or a derivative thereof, (B-2) aluminoxane, and (B-3) a Lewis acid.

13. The propylene copolymer according to claim 12, wherein the transition metal compound represented by the general formula (I) is a transition metal compound represented by the general formula (II):

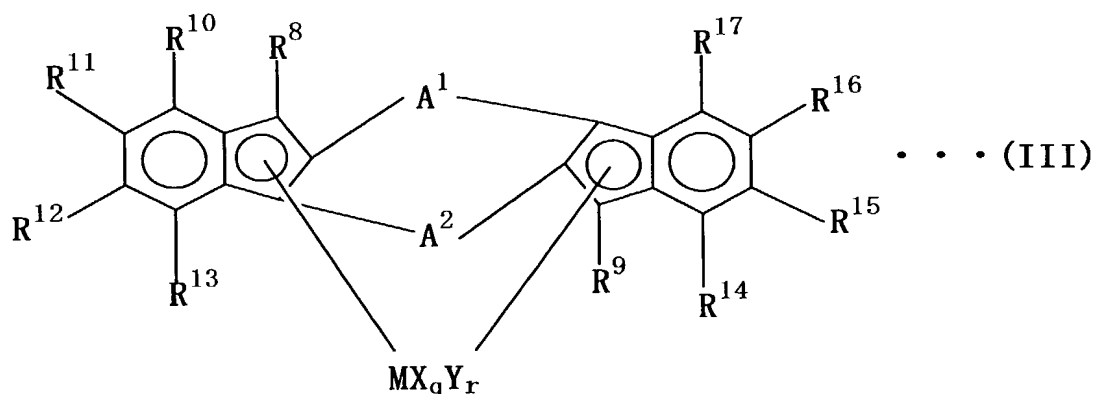
14. The propylene copolymer according to claim 12, wherein the transition metal compound represented by the general formula (I) is a transition metal compound represented by the general formula (II):



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halogen atom, a C<sub>1</sub>-C<sub>20</sub> hydrocarbon group, a C<sub>1</sub>-C<sub>20</sub> halogen-containing hydrocarbon group, a silicon-containing group or a heteroatom-containing group with the proviso that at least one of R<sup>2</sup> through R<sup>7</sup> is a group containing a heteroatom such as oxygen, halogen or silicon; and R<sup>2</sup> through R<sup>7</sup> may be the same or different, and adjacent groups of R<sup>2</sup> through R<sup>7</sup> may be bonded to each other to form a ring.

15. The propylene copolymer according to claim 13, wherein the transition metal compound represented by the general formula (II) is a transition metal compound represented by the general formula (III):



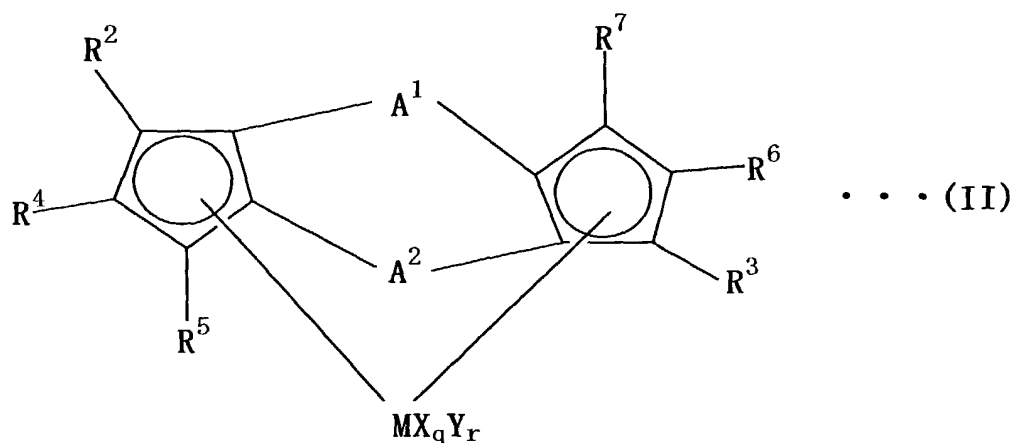
wherein, M, X, Y, A<sup>1</sup>, A<sup>2</sup>, q and r are the same as defined in the above general formula (I); at least one of R<sup>8</sup> and R<sup>9</sup> represents a group containing a heteroatom such as oxygen, halogen or silicon; and R<sup>10</sup> through R<sup>17</sup> are respectively a hydrogen atom, a C<sub>1</sub>-C<sub>20</sub> hydrocarbon group, or a group containing a heteroatom such as oxygen, halogen and silicon.

16. A propylene resin composition comprising the propylene polymer according to claim 1 and a nucleating agent.

17. A propylene resin composition comprising the propylene homopolymer according to claim 3 and a nucleating agent.

18. A propylene resin composition comprising the propylene copolymer according to claim 6 and a nucleating agent.

19. A molded product produced by molding the propylene polymer according to claim 1.
20. A molded product produced by molding the propylene resin composition according to claim 16.
21. A molded product produced by molding the propylene homopolymer according to claim 3.
22. A molded product produced by molding the propylene resin composition according to claim 17.
23. A molded product produced by molding the propylene copolymer according to claim 6.
24. A molded product produced by molding the propylene resin composition according to claim 18.
25. A propylene resin modifier comprising the propylene polymer according to claim 1.
26. A propylene resin modifier comprising the propylene homopolymer according to claim 3.
27. A propylene resin modifier comprising the propylene copolymer according to claim 6.
28. A polymerization catalyst comprising:  
(A') a transition metal compound represented by the general formula (II):

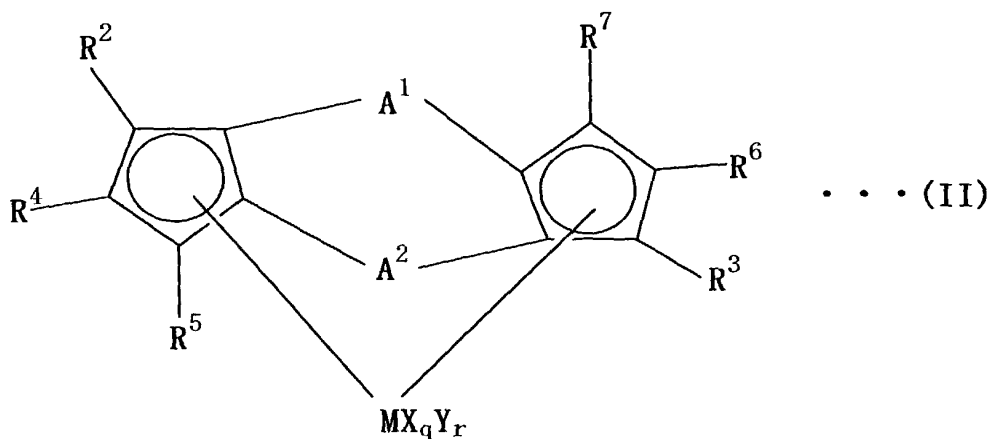


wherein, M, X, Y, A<sup>1</sup>, A<sup>2</sup>, q and r are the same as defined in the above general formula (I); R<sup>2</sup> through R<sup>7</sup> are respectively a hydrogen atom, a halogen atom, a C<sub>1</sub>-C<sub>20</sub> hydrocarbon group, a C<sub>1</sub>-C<sub>20</sub> halogen-containing hydrocarbon group, a silicon-containing group or a heteroatom-containing group with the proviso that at least one of R<sup>2</sup> through R<sup>7</sup> is not a hydrogen atom; and R<sup>2</sup> through R<sup>7</sup> may be the same or different, and adjacent groups of R<sup>2</sup> through R<sup>7</sup> may be bonded to each other to form a ring, and

(B) a component selected from the group consisting of (B-1) a compound capable of forming an ionic complex by reacting with the transition metal compound (A) or a derivative thereof, (B-2) aluminoxane, and (B-3) a Lewis acid.

29. A polymerization catalyst comprising:

(A') a transition metal compound represented by the general formula (II):

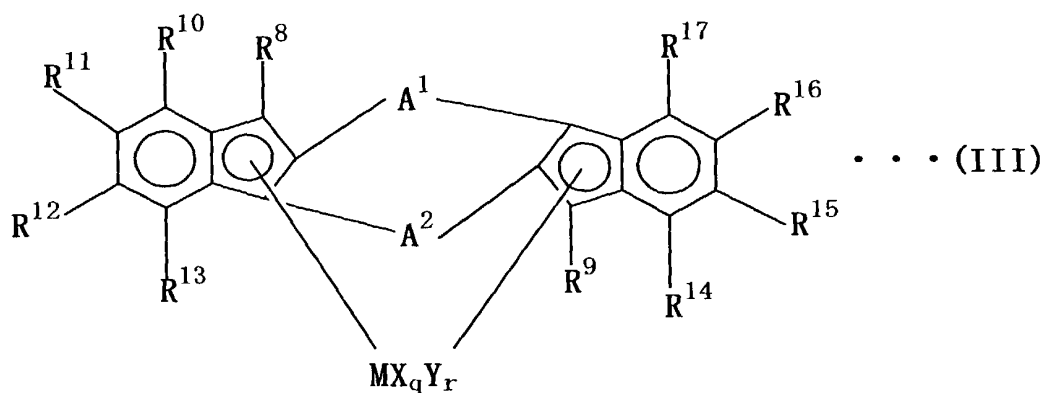


wherein, M, X, Y, A<sup>1</sup>, A<sup>2</sup>, q and r are the same as defined in the above general formula (I); R<sup>2</sup> through R<sup>7</sup> are respectively a hydrogen atom, a halogen atom, a C<sub>1</sub>-C<sub>20</sub> hydrocarbon group, a C<sub>1</sub>-C<sub>20</sub> halogen-containing hydrocarbon group, a silicon-containing group or a heteroatom-containing group with the proviso that at least one of R<sup>2</sup> through R<sup>7</sup> is a group containing a heteroatom such as oxygen, halogen or silicon; and R<sup>2</sup> through R<sup>7</sup> may be the same or different, and adjacent groups of R<sup>2</sup> through R<sup>7</sup> may be bonded to each other to form a ring, and

(B) a component selected from the group consisting of (B-1) a compound capable of forming an ionic complex by reacting with the transition metal compound (A) or a derivative thereof, (B-2) aluminoxane, and (B-3) a Lewis acid.

30. A polymerization catalyst comprising:

(A'') a transition metal compound represented by the general formula (III):



wherein, M, X, Y, A<sup>1</sup>, A<sup>2</sup>, q and r are the same as defined in the above general formula (I); at least one of R<sup>8</sup> and R<sup>9</sup> represents a group containing a heteroatom such as oxygen, halogen or silicon; and R<sup>10</sup> through R<sup>17</sup> are respectively a hydrogen atom, a C<sub>1</sub>-C<sub>20</sub> hydrocarbon group, or a group containing a heteroatom such as oxygen, halogen and silicon, and

(B) a component selected from the group consisting of (B-1) a compound capable of forming an ionic complex by reacting with the transition metal compound (A) or a derivative thereof, (B-2) aluminoxane, and (B-3) a Lewis acid.

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Declaration and Power of Attorney For Patent Application

特許出願宣言書及び委任状

Japanese Language Declaration

日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者（下記の名称が複数の場合）であると信じています。

上記発明の明細書は、

- ☐ 本書に添付されています。
- ☐ \_\_\_\_月\_\_\_\_日に提出され、米国出願番号または特許協定条約国際出願番号を\_\_\_\_とし、  
(該当する場合) \_\_\_\_に訂正されました。

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

私は、連邦規則法典第37編第1条56項に定義されるとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled.

PROPYLENE POLYMER, AND RESIN COMPOSITION

AND MOLDED PRODUCT THEREOF

the specification of which

- ☐ is attached hereto.
- ☒ was filed on 05/10/2000  
as United States Application Number or  
PCT International Application Number  
PCT/JP00/06943 and was amended on  
\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

# Japanese Language Declaration (日本語宣言書)

私は、米国法典第35編119条 (a) - (d) 項又は365条 (b) 項に基づき下記の、米国以外の国の少なくとも一カ国を指定している特許協力条約365 (a) 項に基づく国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している、本出願の前に出願された特許または発明者証の外国出願を以下に、枠内をマークすることで、示しています。

## Prior Foreign Application(s)

外国での先行出願

284608/1999

(Number)  
(番号)

Japan

(Country)  
(国名)

284609/1999

(Number)  
(番号)

Japan

(Country)  
(国名)

043976/2000

Japan

私は、第35編米国法典119条 (e) 項に基づいて下記の米国特許出願規定に記載された権利をここに主張いたします。

(Application No.)  
(出願番号)

(Filing Date)  
(出願日)

私は、下記の米国法典第35編120条に基づいて下記の米国特許出願に記載された権利、又は米国を指定している特許協力条約365条 (c) に基づく権利をここに主張します。また、本出願の各請求範囲の内容が米国法典第35編112条第1項又は特許協力条約で規定された方法で先行する米国特許出願に開示されていない限り、その先行米国出願書提出日以降で本出願書の日本国内または特許協力条約国際提出日までの期間中に入手された、連邦規則法典第37編1条56項で定義された特許資格の有無に関する重要な情報について開示義務があることを認識しています。

(Application No.)  
(出願番号)

(Filing Date)  
(出願日)

(Application No.)  
(出願番号)

(Filing Date)  
(出願日)

私は、私自信の知識に基づいて本宣言書中で私が行なう表明が真実であり、かつ私の入手した情報と私の信じることに基づく表明が全て真実であると信じていること、さらに故意になされた虚偽の表明及びそれと同等の行為は米国法典第18編第1001条に基づき、罰金または拘禁、もしくはその両方により処罰されること、そしてそのような故意による虚偽の声明を行えば、出願した、又は既に許可された特許の有効性が失われることを認識し、よってここに上記のごとく宣誓を致します。

I hereby claim foreign priority under Title 35, United States Code, Section 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

## Priority Claimed

優先権主張

05/10/1999

(Day/Month/Year Filed)  
(出願年月日)

☒ Yes  
はい

☐ No  
いいえ

05/10/1999

(Day/Month/Year Filed)  
(出願年月日)

☒ Yes  
はい

☐ No  
いいえ

22/02/2000

X

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

(Application No.)  
(出願番号)

(Filing Date)  
(出願日)

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code Section 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of application.

(Status: Patented, Pending, Abandoned)  
(現況: 特許許可済、係属中、放棄済)

(Status: Patented, Pending, Abandoned)  
(現況: 特許許可済、係属中、放棄済)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

**Japanese Language Declaration**  
(日本語宣言書)

委任状：私は下記の発明者として、本出願に関する一切の手続きを米特許商標局に対して遂行する弁理士または代理人として、下記の者を指名いたします。  
(弁護士、または代理人の指名及び登録番号を明記のこと)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: (list name and registration number)

Norman F. Oblon, Reg. No. 24,618; Marvin J. Spivak, Reg. No. 24,913; C. Irvin McClelland, Reg. No. 21,124; Gregory J. Maier, Reg. No. 25,599; Arthur I. Neustadt, Reg. No. 24,854; Richard D. Kelly, Reg. No. 27,757; James D. Hamilton, Reg. No. 28,421; Eckhard H. Kuesters, Reg. No. 28,870; Robert T. Pous, Reg. No. 29,099; Charles L. Gholz, Reg. No. 26,395; William E. Beaumont, Reg. No. 30,996; Jean-Paul Lavalleye, Reg. No. 31,451; Stephen G. Baxter, Reg. No. 32,884; Richard L. Treanor, Reg. No. 36,379; Steven P. Weihrouch, Reg. No. 32,829; John T. Goolkasian, Reg. No. 26,142; Richard L. Chinn, Reg. No. 34,305; Steven E. Lipman, Reg. No. 30,011; Carl E. Schlier, Reg. No. 34,426; James J. Kulbaski, Reg. No. 34,648; Richard A. Neifeld, Reg. No. 35,299; J. Derek Mason, Reg. No. 35,270; Surinder Sachar, Reg. No. 34,423; Jeffrey B. McIntyre, Reg. No. 36,867; William T. Enos, Reg. No. 33,128; Michael E. McCabe, Jr., Reg. No. 37,182; Bradley D. Lytle, Reg. No. 40,073; and Michael R. Casey, Reg. No. 40,294, with full powers of substitution and revocation

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単独発明者または第一の共同発明者の氏名	1-00	Full name of sole or first joint inventor <u>Takuji OKAMOTO</u>
発明者の署名	日付	Inventor's signature <u>Takuji Okamoto</u> Date March 4, 2002
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国籍		Citizenship <u>Japan</u>
郵便の宛先		Post Office Address <u>1-1, Anesakikaigan, Ichihara-shi, Chiba,</u>
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第二の共同発明者の氏名	2-00	Full name of second joint inventor, if any <u>Takashi KASHIWAMURA</u>
第二の共同発明者の署名	日付	Second joint Inventor's signature <u>Takashi Kashiwamura</u> Date March 4, 2002
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		<u>Japan</u>

(第三以降の共同発明者についても同様に記載し、署名すること)

(Supply similar information and signature for third and subsequent joint inventors.)

Japanese Language Declaration  
(日本語宣言書)

第三の共同発明者の氏名	3-00	Full name of third joint inventor, if any Noriyuki TANI
第三の共同発明者の署名	日付	Third joint inventor's signature Noriyuki Tani Date March 4, 2002
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第四の共同発明者の氏名	4-00	Full name of fourth joint inventor, if any Yutaka MINAMI
第四の共同発明者の署名	日付	Fourth joint inventor's signature Yutaka Minami Date March 4, 2002
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第五の共同発明者の氏名	5-00	Full name of fifth joint inventor, if any Masami KANAMARU
第五の共同発明者の署名	日付	Fifth joint inventor's signature Masami Kanamaru Date March 4, 2002
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第六の共同発明者の氏名	6-00	Full name of sixth joint inventor, if any Koji KAKIGAMI
第六の共同発明者の署名	日付	Sixth joint inventor's signature Koji Kakigami Date March 4, 2002
住所		Residence Chiba, Japan JPX
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